A synthetic, structural and reactivity study of [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$X)] complexes, R = Me or Et; X = CHO, CH=CHFc, CH=CH(η^5-C$_5$H$_4$)Co(η^4-C$_4$Ph$_4$), CH=C(CN)$_2$: Unexpected formation of [(η^5-cyclopentadienyl)-(η^4-3,4,5,6-tetraethyl-α-pyrone)cobalt]

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ABSTRACT

The tetraethyl- and tetramethyl-cyclobutadiene complexes [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$CHO)] R = Et, **5**, R = Me, **7**, and [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$CO$_2$Me)] R = Et, **6**, R = Me, **8**, are conveniently prepared by photolysis of the corresponding isocobaltocenium cations [(η^4-C$_4$R$_4$)Co(η^6-C$_6$H$_5$Me)]$^+$ in acetonitrile, and subsequent treatment with Na[C$_5$H$_4$CHO] or Na[C$_5$H$_4$CO$_2$Me]. The aldehydes **5** and **7** undergo Wittig and Knoevenagel reactions with [FcCH$_2$PPh$_3$]I and CH$_2$(CN)$_2$, to form [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$CH=CHFc)] and [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$CH=C(CN)$_2$)], **11** and **15**, respectively. The Horner-Wittig reaction of [(η^4-C$_4$R$_4$)Co(η^5-C$_5$H$_4$CH$_2$P(=O)(OEt)$_2$] with [(η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$CHO)] yields [(η^4-C$_4$R$_4$)Co(η^5:η^5-C$_5$H$_4$CH=CH–C$_5$H$_4$)Co(η^4-C$_4$Ph$_4$)], **12** and **13**. [(η^4-C$_4$Me$_4$)Co(η^5-C$_5$H$_4$CHO)] also reacts with *t*-BuLi and FcLi to furnish the corresponding secondary alcohols, **16** and **17**, respectively. Surprisingly, the attempted direct synthesis of **5** by reaction of Na[C$_5$H$_5$] and ethyl formate with [(η^4-C$_4$Et$_4$)Co(CO)$_2$I], **1**, instead yielded [(η^5-C$_5$H$_5$)Co(η^4-3,4,5,6-tetraethyl-α-pyrone)], **18**, and a mechanistic proposal is advanced. The X-ray crystal structures of **1**, **7**, **8**, **11**(*Z*), **15** and **18**, and also the isocobaltocenium salts [(η^4-C$_4$Et$_4$)Co(η^6-C$_6$H$_5$Me)][PF$_6$], **2**, and [(η^4-C$_4$Et$_4$)Co(η^6-1,3,5-C$_6$H$_3$Me$_3$)][PF$_6$], **4**, are reported.

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1. Introduction

In continuation of our recent reports on the chemistry and non-linear optical properties of [(η^5-C$_5$H$_5$)Co(η^4-C$_4$Ph$_4$)] and its derivatives [1–3], it seemed appropriate to extend these studies to include other [(η^5-C$_5$H$_4$X)Co(η^4-C$_4$R$_4$)] complexes where R = Me or Et. The replacement of the C$_4$Ph$_4$ moiety by C$_4$Me$_4$ or C$_4$Et$_4$ renders the cyclobutadiene ring more electron-rich, as both methyl and ethyl groups are electron-donating while phenyl is comparatively electron-withdrawing with σ^* values of 0.00, −0.10 and 0.75, respectively, (where *H* = 0.49) [4]. Furthermore, the replacement of aryl by alkyl groups precludes any π-interactions which may have existed between the cyclobutadiene and the phenyl groups.

The first tetramethylcyclobutadiene metal complex – [(η^4-C$_4$Me$_4$)NiCl$_2$]$_2$ – was reported by Criegee and Schröder in 1959 [5]; in the same year, Markby et al. [6] unsuccessfully attempted to prepare [(η^5-cyclopentadienyl)(η^4-tetramethylcyclobutadiene)cobalt], [(η^5-C$_5$H$_5$)Co(η^4-C$_4$Me$_4$)], from [(η^5-C$_5$H$_5$)Co(CO)$_2$]

[7] and 2-butyne. However, it was almost a decade later that Bruce and Maitlis used [(η^4-C$_4$Me$_4$)NiCl$_2$]$_2$ to prepare a variety of [Co(η^4-C$_4$Me$_4$)] complexes including [(η^5-C$_5$H$_5$)Co(η^4-C$_4$Me$_4$)] [8], as shown in Scheme 1. Since then, a wide range of tetramethylcyclobutadiene cobalt compounds have been prepared including, among others, boratobenzene [9], cyclopentadienyl, indenyl and fluorenyl [10], carboranes [11] and triple-decker complexes [12], and this area has been comprehensively reviewed [13]. Nevertheless, despite the extensive researches carried out on [Co(η^4-C$_4$Me$_4$)] complexes, comparatively few studies have been conducted on their tetraethylcyclobutadiene analogues [14–16]. We here describe the synthesis, X-ray crystallographic characterization, and reactivity of several new (η^4-tetraethylcyclobutadiene)cobalt and (η^4-tetramethylcyclobutadiene)cobalt complexes.

2. Results and discussion

(η^4-C$_4$Ph$_4$) complexes of Co^{III}, such as [(η^5-C$_5$H$_5$)Co(η^4-C$_4$Ph$_4$)], are most conveniently prepared by the thermal dimerisation of diphenyl acetylene, PhC≡CPh, using suitable cyclopentadienyl–cobalt substrates such as [(η^5-C$_5$H$_5$)Co(C$_2$H$_2$)$_2$] [16], [(η^5-C$_5$H$_5$)$_2$Co] [17], [(η^5-C$_5$H$_5$)Co(CO)$_2$] [18], [(η^5-C$_5$H$_5$)Co(η^4-COD)]

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Scheme 1. The first preparation of $[(\eta^5-C_5H_5)Co(\eta^4-C_4Me_4)]$.

[19] or $[(\eta^5-C_5H_5)Co(PPh_3)_2]$ [20]. However, this requires relatively high temperatures, e.g. refluxing toluene or xylene, and is less suitable for volatile alkynes such as 2-butyne and 3-hexyne. For these a more efficient route to $(\eta^4-C_4Me_4)Co$ or $(\eta^4-C_4Et_4)Co$ complexes is that described by Herberich, Koelle, et al. [21]. In this one pot reaction (Scheme 2), aluminium trichloride (Al_2Cl_6) reacts with two equivalents of alkyne to give a σ-bonded aluminium–cyclobutadiene complex that has been characterised by X-ray crystallography [22]. When this material is treated with dicobalt octacarbonyl, the C_4Me_4 (or C_4Et_4) ligand migrates to cobalt to form a $[(\eta^4-C_4R_4)Co(CO)_3]^+$ salt [23]; subsequent reaction with trimethylamine N-oxide and sodium iodide furnishes $[(\eta^4-C_4R_4)Co(CO)_2I]$.

Surprisingly perhaps, the crystal structure of $[(\eta^4-C_4Et_4)Co(CO)_2I]$, **1**, has not previously been reported, and is shown in Fig. 1. The molecule adopts a piano stool structure with Co–Cb(centroid) and Co–C(Cb) distances of 1.760(1) and 2.0248(18)–2.0488(17) respectively. These are the longest such distances observed of the C_4Et_4 complexes reported herein. The I–Co–CO angles were found to be 96.92(6)° and 94.15(6)° while the OC–Co–CO angle is 99.79(9)°. These angles are larger than those found in other $[(C_5R_5)M(CO)_2L]$ complexes, where M = Fe, R = H or Me, and L = I, $SnCl_3$ or $SnCl_2Ph$ [24–27]. In **1**, all three ligands make an angle of between 119.60(1)° and 120.72(6)° with the metal and the centroid of the cyclobutadiene ligand. These angles are smaller than what has been recorded for other isoelectronic analogues, and it appears that they are a consequence of the size of the carbocycle rather than of the other ligands.

2.1. Syntheses of the isocobaltocenium salts (2–4)

Although these iodo complexes might have been expected to behave as ideal precursors for $[(\eta^5-C_5H_4X)Co(\eta^4-C_4R_4)]$ derivatives, their reactions with substituted sodium cyclopentadienides, $Na[C_5H_4X]$, often proceed in low yields, especially when R = Et (Scheme 3, Route 1). In practice a less direct route proved more useful. The reactions of $[(\eta^4-C_4R_4)Co(CO)_2I]$ with excess Al_2Cl_6 in refluxing arenes yield salts of the isocobaltocenium ions, $[(\eta^4-C_4R_4)Co(\eta^6-arene)]^+$; these cations can be isolated as PF_6^- salts. Isometallocenes are compounds in which the metal is π-bonded to both cyclobutadiene and arene residues. Those of cobalt were first described by Maitlis and Efraty in 1965 [28]. They are best prepared by the method described above, but have also been prepared from η^3-cyclobutenonylcobalt complexes [29]. In the intervening years many isometallocenes, incorporating a wide range of metal centres, have been described [29–32]. In 1987, Pauson et al. reported a series of (tetramethylcyclobutadiene)isocobaltocenium salts of the general formula $[(\eta^4-C_4Me_4)Co(\eta^6-arene)]^+$ [33]. These were prepared by refluxing $[(\eta^4-C_4Me_4)Co(CO)_2I]$ in the presence of a three-fold excess of $AlCl_3$ in the appropriate aromatic reagent,
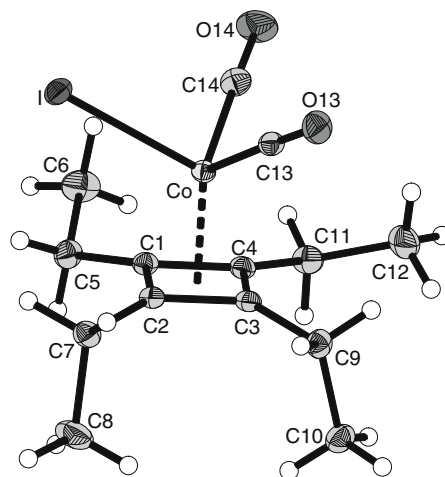
Fig. 1. X-ray crystal structure of $[(\eta^4-C_4Et_4)Co(CO)_2I]$, **1**. Thermal ellipsoids are drawn at the 50% probability level.
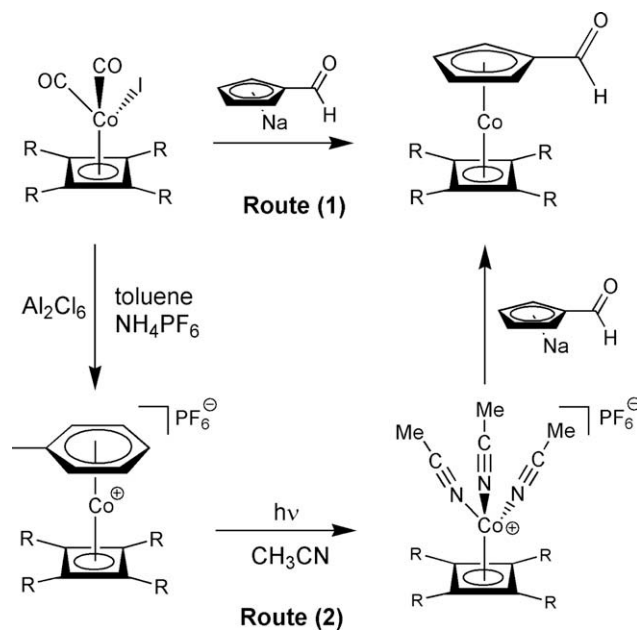
Scheme 3. Synthetic strategies towards $[(\eta^5-C_5H_4CHO)Co(\eta^4-C_4R_4)]$.

which served as both the solvent and as a ligand source. Addition of NH_4PF_6 precipitated the pale yellow salts from solution. These isometallocenes are air stable but their arene substituents are readily replaceable. Upon photolysis in acetonitrile, they lose the arene ligand to form $[(\eta^4-C_4Me_4)Co(CH_3CN)_3]^+$ salts which are not isolated but instead are treated with $Na[C_5H_4X]$ to give the $[(\eta^5-C_5H_4X)Co(\eta^4-C_4Me_4)]$ complexes in good yield (see Scheme 3, Route 2). To this end, they have been successfully incorporated
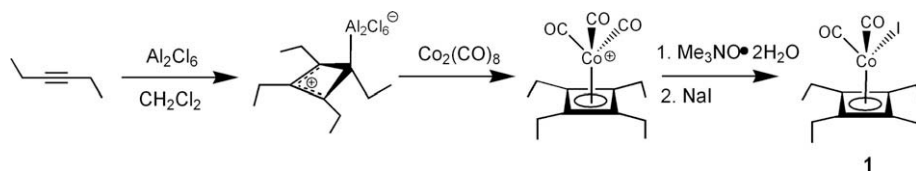
Scheme 2. Synthesis of $[(\eta^4-C_4Et_4)Co(CO)_2I]$, **1**.

Fig. 2. X-ray crystal structures of the cationic components in [(η^6-toluene)Co(η^4-C$_4$Et$_4$)] [PF$_6$], **2**, and [(η^6-mesitylene)Co(η^4-C$_4$Et$_4$)] [PF$_6$], **4**. Thermal ellipsoids are drawn at the 15% (**2**) and 50% (**4**) probability level.

in stacking reactions [32], and other ligand displacement processes [10].

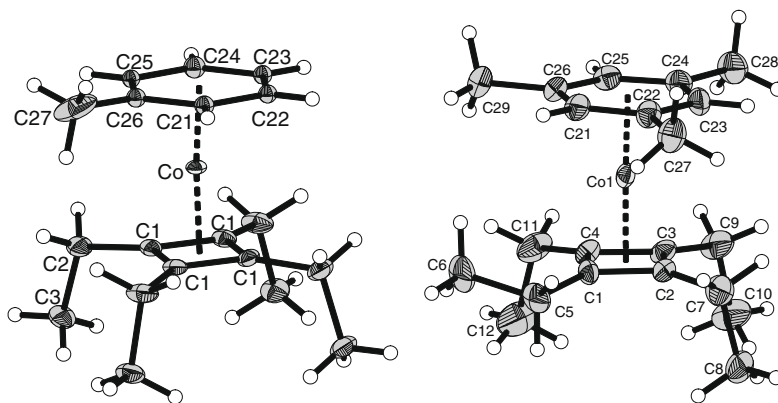The isocobaltocenium salts [(η^6-arene)Co(η^4-C$_4$Et$_4$)][PF$_6$], where arene = toluene, **2**, *p*-xylene, **3**, and mesitylene, **4**, were prepared by refluxing **1** with excess Al$_2$Cl$_6$ in the appropriate aromatic solvent. In all cases, pale yellow crystals were precipitated with ether from acetone solutions, and the X-ray crystal structures of the cationic components of complexes **2** and **4** appear as Fig. 2. The structures reveal some interesting variations in bond lengths and angles. Two independent cations and anions per unit cell are observed in the structure of the mesitylene complex, **4**. The cobalt–C(Me) bond lengths (average 2.126 Å) are longer than the cobalt–C(H) distances (average 2.109 Å), and the C(H)–C(Me)–C(H) angles (average 118.6°) are noticeably smaller than the C(Me)–C (H)–C(Me) angles (average 121.4°) in the mesitylene ring. Unfortunately, because of crystallographic disorder in the toluene complex, **2**, no direct comparison can be made with **4**, although Kennedy and Pauson [34] had reported a similar elongation of an amine-substituted Co–carbon bond (Co–C(NEt$_2$)) forcing the Co atom away from the centre of the C$_6$H$_5$NEt$_2$ ring.

Apparently, increased methylation of the arene ring renders the ligand more electron-rich and increases its ring-to-metal bonding interaction. The less electropositive metal centre is therefore less able to accept electron density from the C$_4$Et$_4$ ligand. This reduction is manifested in an increase in the cobalt-to-Cb(centroid) distances from 1.696(1) Å in **2** to 1.710(3) Å in **4**, and is further reflected in the ^{13}C NMR spectra of the respective complexes. The C–C bond lengths within the carbocyclic ligands are normal [31].

In **2**, which has a crystallographically imposed fourfold axis, all the ethyl substituents in the cyclobutadiene ring are oriented axially (distal) with respect to the metal; in contrast, in both cations of **4**, three of the ethyl groups are likewise distal while the fourth is twisted almost perpendicular to the others in a more equatorial configuration.

2.2. Syntheses of [(η^5-C$_5$H$_4$R)Co(η^4-C$_4$Et$_4$)], R = CHO, (**5**), and CO$_2$Me (**6**)

As noted already in Scheme 3, [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Me$_4$)], had successfully been prepared by both Route 1 and Route 2, with insignificant differences between the overall yields [10]. However, in the case of [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Et$_4$)], **5**, we found Route 2 (via the arene and acetonitrile intermediate complexes) to be a more effective synthetic route. Although it required several steps, and was more time consuming, the overall yield (50%) was substantially higher than for the more direct Route 1, which in our hands gave only a 13% yield. Hence, the aldehyde, **5**, and the methyl ester, **6**, were both prepared by irradiation of the toluene–isocobaltocenium complex, **2**, in CH$_3$CN. Replacement of the η^6-arene ligand by three acetonitrile ligands was accompanied by a change from a yellow slurry to a dark red solution. However, this complex was not isolated, but rather was added directly to a solution of the appropriate sodium cyclopentadienide salt. Once mixed, the reaction is complete within 2 h and the products were separated by column chromatography on alumina, as silica seemed to promote their decomposition. The η^4-C$_4$Et$_4$ complexes **5** and **6**

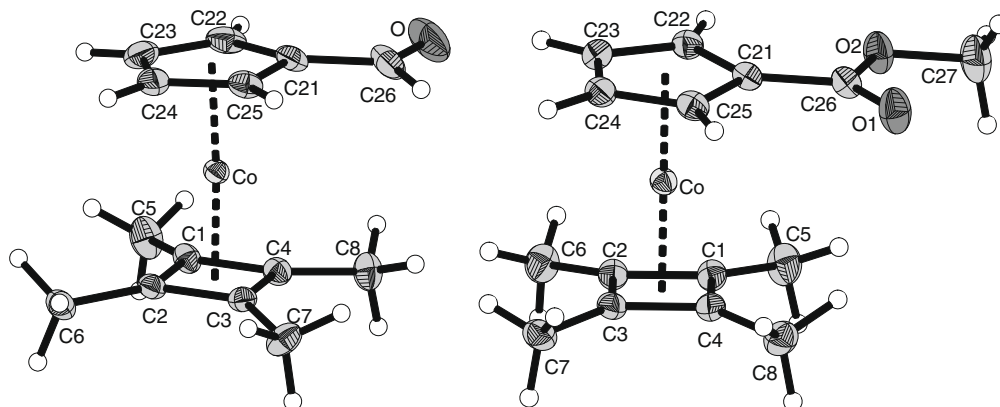**Fig. 3.** X-ray crystal structures of [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Me$_4$)], **7**, and [(η^5-C$_5$H$_4$CO$_2$Me)Co(η^4-C$_4$Me$_4$)], **8**. Thermal ellipsoids are drawn at the 50% (**7**) and 25% (**8**) probability levels.

are unstable in air and in solution, and gradually decompose even at −10 °C. They are oils at room temperature but may solidify at lower temperatures.

The corresponding tetramethylcyclobutadiene complexes [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Et$_4$)], **7**, and [(η^5-C$_5$H$_4$CO$_2$Me)Co(η^4-C$_4$Et$_4$)], **8**, were likewise prepared via Route 2 from the [Co(η^4-C$_4$Me$_4$)(η^6-C$_6$H$_5$CH$_3$)]$^+$ cation. In marked contrast to their η^4-C$_4$Et$_4$ analogues, both **7** and **8** are stable in air, and are low melting orange solids that can be purified either by sublimation or by column chromatography; their molecular structures are shown in Fig. 3. As with their C$_4$Ph$_4$ analogues [1], the Co–Cp(centroid) distances (1.671(2) Å in **7**, 1.677(1) Å in **8**) are noticeably shorter than are the Co–Cb(centroid) distances (1.683(2) Å in **7**, 1.683(1) Å in **8**); these data parallel those previously observed in the acetyl complex [(η^5-C$_5$H$_4$COMe)Co(η^4-C$_4$Me$_4$)] [10].

2.3. Reactions of the [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$R$_4$)] complexes (R = Et) (5) and (R = Me) (7)

As summarised in Scheme 4, the aldehyde complexes, **5** and **7**, underwent characteristic reactions including reduction, condensation and coupling reactions; however, because of the limited thermal stability of **5**, it had to be freshly prepared immediately prior to use. Addition of sodium borohydride to the aldehyde, **5**, or lithium aluminium hydride to the methyl ester, **6**, reduced them to the corresponding primary alcohol, **9**, which, like its precursors, is also air sensitive. The phosphonate **10** was prepared by reaction of the alcohol, **9**, with diethyl phosphite and sodium [35,36], but it was very unstable and failed to react with ketones in a satisfactory manner.

Nevertheless, the aldehyde **5** was used successfully in the Wittig [37] and Horner-Wittig [38] coupling reactions. With ferrocenylmethyltriphenylphosphonium iodide [39], it gave both Z and E isomers of [η^5-(2-ferrocenylethenyl)cyclopentadienyl](η^4-tetraethylcyclobutadiene)cobalt, **11**, as stable solids; the identity of the Z isomer was established by X-ray crystallography. The (tetraethylcyclobutadiene)- and (tetramethylcyclobutadiene)-dicobalt stilbenes, **12** and **13**, were prepared by allowing [(η^5-diethylphosphonatomethylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene) cobalt] to react with (η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$R$_4$), **5** (R = Et), or **7** (R = Me), respectively, in a Horner–Wittig process. As is commonly the case, only the E isomers of **12** and **13** were obtained. The aldehydes **5** and **7** also reacted with malononitrile in a Knoevenagel condensation [40] using triethylamine as a base to give the 2,2-dicyanovinyl derivatives **14** and **15**, respectively. These latter dark red crystalline materials are stable both in air and in solution. [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Me$_4$)], **7**, is also susceptible to nucleophilic attack by organolithium reagents such as ferrocenyl-lithium and tert-butyl-lithium and gave rise to the corresponding chiral secondary alcohols **16** and **17** respectively. The complexes **11**(**Z**) and **15** were unambiguously characterised by X-ray crystallography, and their structures appear in Figs. 4 and 5.

Two independent molecules were observed in the unit cell of the iron–cobalt double sandwich compound, **11**(**Z**), and the ferrocenyl unit is twisted out of the cyclopentadienyl–cobalt plane by 51.5(2)° and 44.6(2)° in the two cases. As with the C$_4$Me$_4$ complexes **7** and **8**, the Co–Cp(centroid) distances in **11**(**Z**) (1.667(2) and 1.676(1) Å) are noticeably shorter than are the Co–Cb(centroid) distances (1.681(2) and 1.685(1) Å). Interestingly, the iron-to-cyclopentadienyl distances in **11**(**Z**) are quite different in one
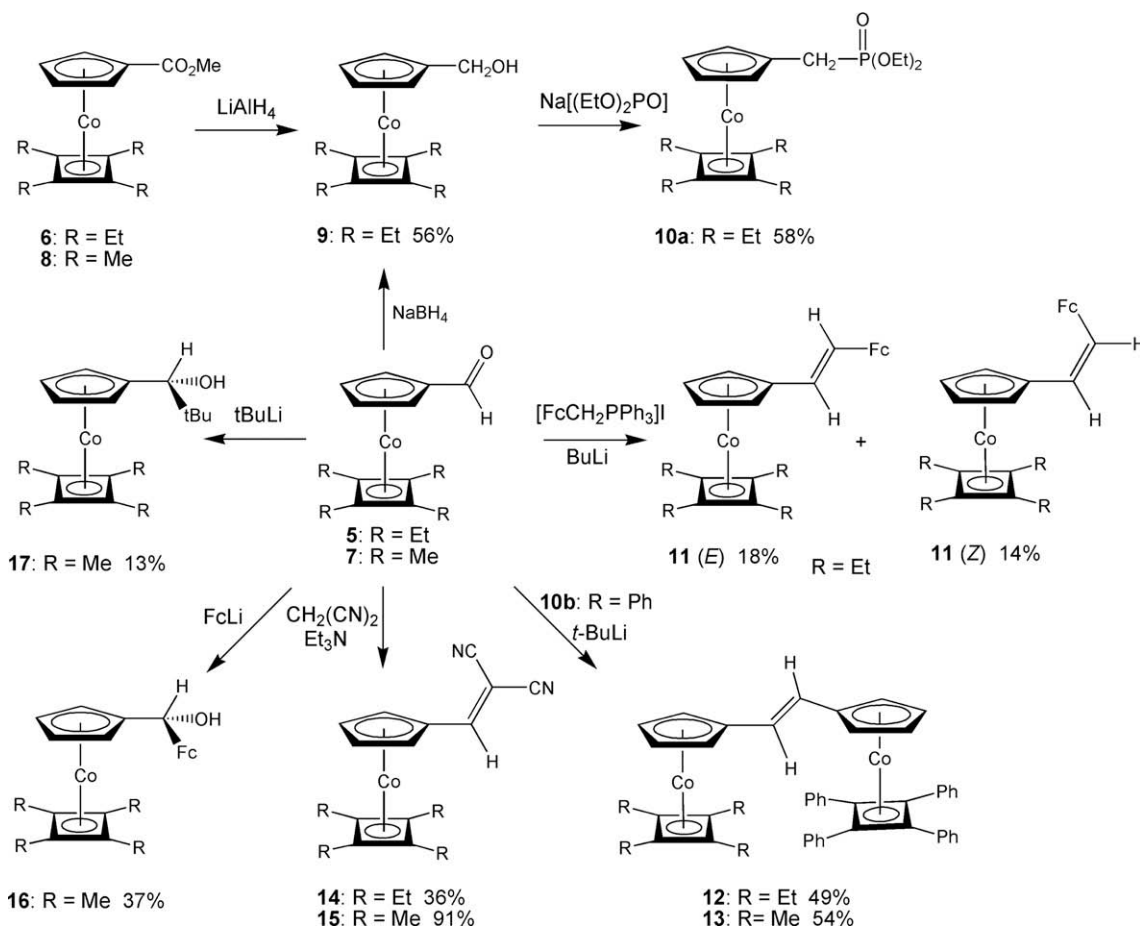
Scheme 4. Reactions of [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$R$_4$)].
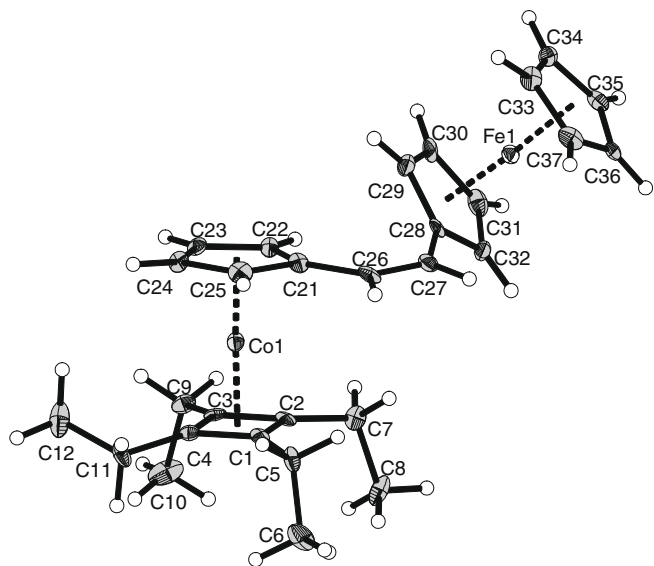
Fig. 4. X-ray crystal structure of $(\eta^4\text{-}C_4Et_4)Co(\eta^5\text{:}\eta^5\text{-}C_5H_4CH=CHC_5H_4)Fe(\eta^5\text{-}C_5H_5)$, **11(Z)**. Thermal ellipsoids are drawn at the 50% probability level.
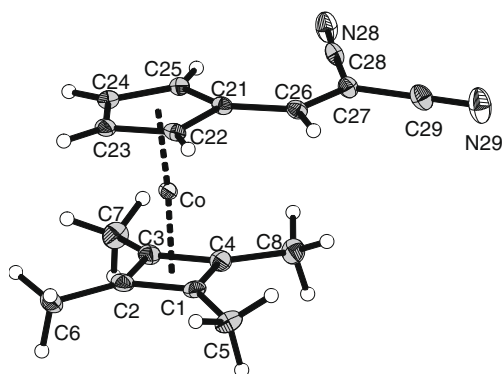
Fig. 5. X-ray crystal structure of $[(\eta^5\text{-}C_5H_4CH=C(CN)_2)Co(\eta^4\text{-}C_4Me_4)]$, **15**. Thermal ellipsoids are drawn at the 50% probability level.

molecule – Fe–C_5H_4(centroid) 1.638(1) vs. Fe–C_5H_5(centroid) 1.652(1) – whereas they are not significantly different (1.640(2) and 1.646(2) Å) in the other. As with $[(\eta^6\text{-mesitylene})Co(\eta^4\text{-}C_4Et_4)]^+$, **4**, three of the ethyl groups are oriented axially distal while the fourth is rotated almost proximal.

The metrical parameters of the 2,2-dicyanovinyl complex **15** parallel closely those of the methyl ester, **8**, with Co–Cp(centroid) and Co–Cb(centroid) distances of 1.676(1) Å and 1.685(1) Å, respectively. The =$C(CN)_2$ moiety is coplanar with the Cp(H)C= fragment, and in this case, as with the others reported herein, the angle Cp(centroid)–Co–Cb(centroid) lies in the range 176–180°.

The striking difference in stability between the tetraethyl- and tetramethyl-cyclobutadiene–cobalt complexes merits comment. One might suspect that the presence of β-hydrogens in the ethyl groups may lead to loss of ethylene via a cobalt hydride, and experiments to test this hypothesis are continuing.

2.4. Unexpected formation of $[(\eta^5\text{-cyclopentadienyl})\{\eta^4\text{-}(3,4,5,6\text{-}tetraethyl–pyrone)\}cobalt]$ (**18**)

During the synthesis of $[(\eta^5\text{-}C_5H_4CHO)Co(\eta^4\text{-}C_4Et_4)]$, **5**, via Route 1, for which the first step is the reaction of sodium

cyclopentadienide with ethyl formate, an unexpected minor side product was characterised by X-ray crystallography as the tetraethyl-α-pyrone complex, **18**. Certainly, pyrones are well-known ligands: (α-pyrone)$Fe(CO)_3$ was generated as a side-product in the preparation of $[(\eta^4\text{-}C_4H_4)Fe(CO)_3]$ from $Fe(CO)_5$ and a cyclobutene complex [41], and as the main product from the reaction of α-pyrone and $Fe(CO)_5$; numerous other preparations have also been described [42–48]. Although the generation of cyclobutadienes by elimination of carbon dioxide from α-pyrones is well established [48,49], the reverse process would appear to be less viable. However, Gleiter has reported the conversion of cobalt-complexed cyclobutadienes into pyridines [50] or cyclopentadienones [51].

The structure of **18** appears as Fig. 6, and clearly indicates the envelope conformation of the η^4-bonded tetraethyl-α-pyrone ligand. The C_4Et_4 unit deviates from parallelism with the C_5H_5 ring by 7°, and the angle C_4Et_4(centroid)–Co–C_5H_5(centroid) is 172.7°. The interplanar angle between the tetraethylbutadiene moiety and the CO_2 fragment is 42.7°, similar to the fold angles previously observed (40–42°) in other (α-pyrone)$Fe(CO)_3$ and (α-pyrone)-$Co(C_5H_5)$ complexes [43,52–54]. As seen in molecules **4** and **11(Z)**, three of the ethyl substituents are oriented axially distal while the fourth is rotated almost into the plane of the butadiene.

The most likely source of the additional CO_2 moiety is ethyl formate, and Scheme 5 illustrates a proposed mechanistic scenario that invokes initial displacement of iodide by excess cyclopentadienide, the stepwise reaction of ethyl formate to give a cycloadduct, **19**, followed by an electrocyclic ring opening to the η^4-2-ethoxy-2H-pyran complex, **20**. (Precedent for the proposed stepwise addition of ethyl formate is provided by the observation [55] that hexafluoroacetone adds to $(\eta^4\text{-tetramethylcyclobutadiene})Fe(CO)_3$ to form $(\eta^3\text{-tetramethylcyclobutadienyl})Fe(CO)_3[(O\text{-}C(CF_3)_2]$, as depicted in Scheme 6.) Finally, conversion of the pyran, **20**, into the pyrone complex, **18**, requires elimination of the components of ethane: this could be readily accomplished through nucleophilic attack by the previously released iodide on the ethoxy substituent thus forming, after tautomerisation, the (η^5-cyclopentadienyl)cobalt(η^4-hydroxypyrylium) anion, **21**, whereby the cobalt formally possesses 20 valence electrons. Such a complex would very readily undergo oxidation to the corresponding 18-electron system, **22**, that loses a proton to yield the observed product, **18**. Thus, the loss of the components of ethane is achieved sequentially by removal of an ethyl cation (as ethyl iodide) with subsequent elimination of hydride (as a proton) after oxidation at cobalt.
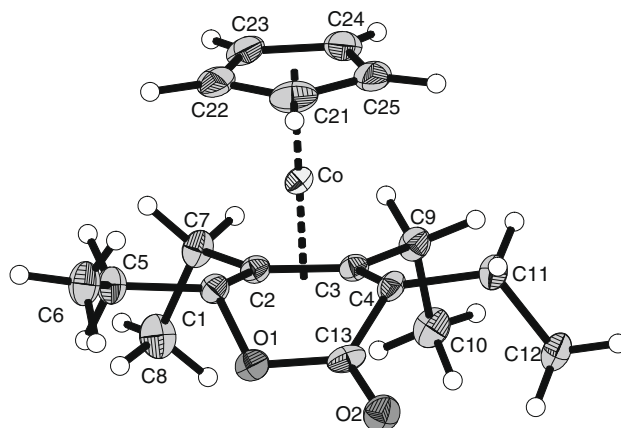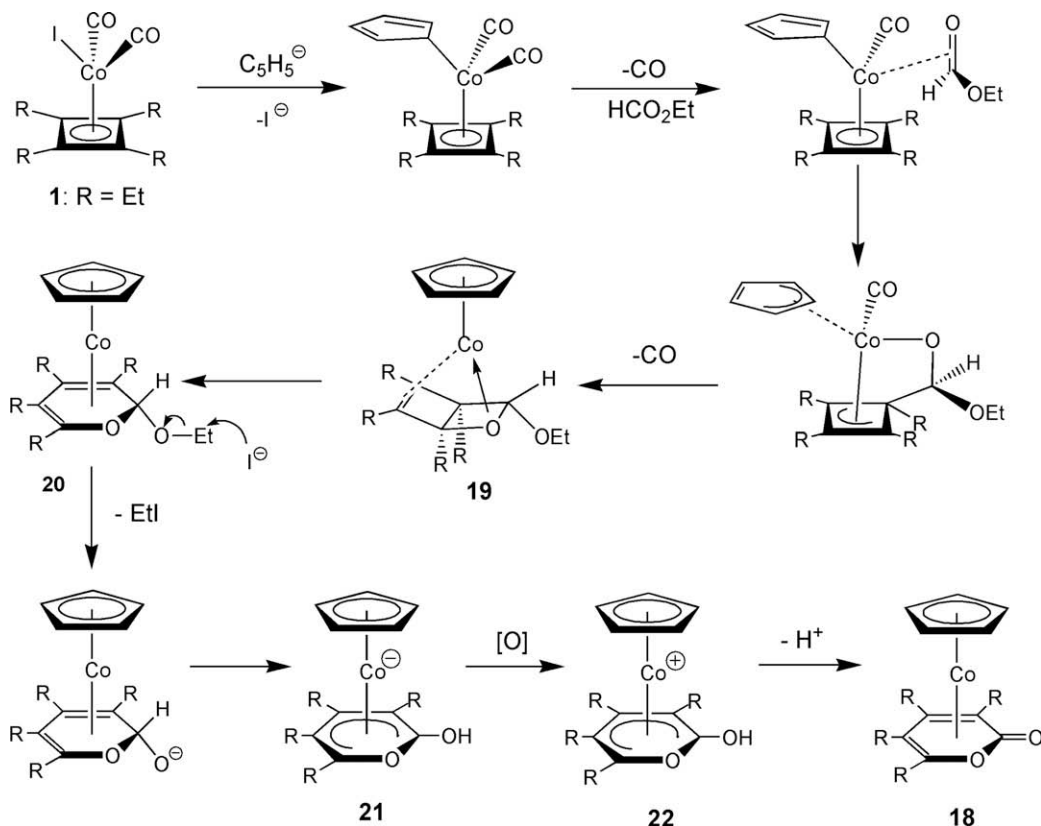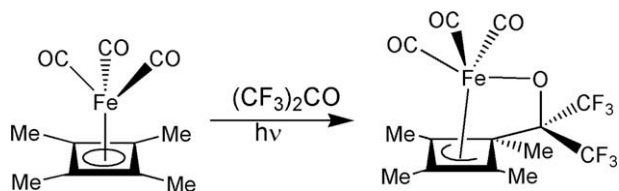

Fig. 6. X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Et_4CO_2]$, **18**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 5. Proposed mechanism for the formation of the (tetraethyl-α-pyrone) Co(C$_5$H$_5$) complex, **18**.

Scheme 6. Reaction of (η^4-C$_4$Me$_4$)Fe(CO)$_3$] with hexafluoroacetone (from Ref. [55]).

2.5. Spectroscopic data

The ^{1}H NMR spectra of the C$_4$Et$_4$-isocobaltocenium salts, **2**, **3** and **4**, exhibit aromatic and methyl proton resonances at δ 6.47–6.09 and δ 2.39–2.32, respectively. Both absorptions are slightly shielded with increased methylation of the C$_6$H$_{6-n}$(CH$_3$)$_n$ ring. A similar trend was previously observed for the C$_4$Me$_4$ derivatives [33]. In **11**, the Fe–C$_5$H$_4$ resonances are assumed to be at lower frequency than the Co–C$_5$H$_4$ absorptions; however, the cyclopentadienyl resonances of the dicobalt–stilbene complexes, **12** and **13**, could not be explicitly distinguished from each other. The alkene protons of **12** and **13** give rise to a pair of doublets, with ^3J(H–H)

coupling constants of 12 Hz for the *cis* isomer complex **11(Z)**, and 16 Hz for the *trans* complexes **12(E)** and **13(E)**. In the α-pyrone complex, **18**, the intrinsic planar chirality renders the CH$_2$ protons of the ethyl groups diastereotopic. As such, each methylene proton of the four ethyl groups is observed as a doublet of quartets arising from the vicinal and geminal couplings.

Similar trends are observed in the ^{13}C NMR spectra of the toluene, *p*-xylene and mesitylene isocobaltocenium salts, **2**, **3** and **4**, respectively. The carbon resonances of the cyclobutadiene ring, the methylene carbons of the C$_4$Et$_4$ ligand and the methyl groups of the C$_6$H$_{6-n}$(CH$_3$)$_n$ ligands are all shielded with increased methylation of the aromatic ring. This shift is most pronounced for the C$_4$ resonances: 97.0 ppm in **2**, 95.7 ppm in **3**, and 94.4 ppm in **4**. In general, the chemical shifts of the cyclobutadiene ring carbons of the (η^4-C$_4$Me$_4$)-cobalt complexes lie between the corresponding resonances of the C$_4$Ph$_4$ and C$_4$Et$_4$ complexes.

The infrared spectrum of [(η^4-C$_4$Et$_4$)Co(CO)$_2$I], **1**, exhibits v(CO) peaks at 2048 and 2008 cm^{-1} in dichloromethane, and 2049 and 2011 cm^{-1} in KBr. These frequencies are almost identical to those of their tetramethyl analogues, but slightly lower than their tetraphenyl counterparts, and are comparable to the values reported for [(η-C$_5$H$_5$)Fe(CO)$_2$I] (2044 and 2000 cm^{-1}) [56]. The esters **6** and **8** absorb at 1705 cm^{-1} and 1701 cm^{-1}, respectively, while the

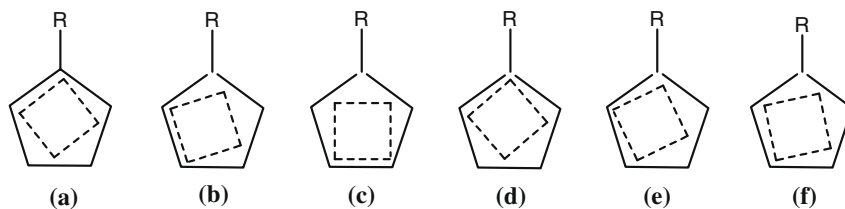**Fig. 7.** Orientations of the C$_4$ ligand relative to the C$_5$H$_4$R ring.

aldehyde $v(CO)$ resonances in **5** and **7** are found at 1674 cm^{-1} and 1670 cm^{-1}.

2.6. Relative orientations of the cyclopentadienyl and cyclobutadiene rings

The cyclopentadiene ligands of the ferrocenyl groups in **11**(Z) are slightly staggered, however, as depicted in Fig. 7, one can envisage six different orientations of the substituted cobalt C_5H_4R ligand relative to the cyclobutadiene ring [3]. The rings may be oriented so that one of the C–C bonds on the C_4 ring lies parallel to one of three different C–C bonds of the C_5H_4R ((a)–(c)), or they may be positioned such that a carbon of the C_4 ligand eclipses one of the C_5H_4R atoms ((d)–(f)). Conformations (c) and (f) are observed for the two independent molecules of **11**(Z). The [Co(η^5-C_5H_4X)(η^4-C_4Me_4)] complexes **6**, **8** and **15** adopt orientations (d), (c) and (c) respectively, while the acetyl derivative [10] also adopts (c).

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Varian 300 MHz or 600 MHz spectrometers. Assignments were based on standard 2-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and HMBC, NOESY). Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Melting points were determined on an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

3.2. Preparation of iodo(η^4-tetraethylcyclobutadiene)dicarbonylcobalt (**1**)

A solution of 3-hexyne (3.50 g, 42.6 mmol) in dry dichloromethane (25 mL) was added dropwise to a suspension of aluminium chloride (6.25 g, 46.9 mmol) in dry dichloromethane (40 ml) over 45 min. Dicobalt octacarbonyl (3.64 g, 10.7 mmol) was added after 1 h, and the resulting solution stirred at room temperature for 4 days. The mixture was poured slowly onto ice (30 mL) and stirred for a further hour. The aqueous layer was separated, filtered and sodium iodide dihydrate (3.97 g, 21.3 mmol) and trimethylamine N-oxide dihydrate (2.37 g, 21.3 mmol) were added with stirring. After 1 h the brown precipitate was filtered off, dissolved in dichloromethane and filtered through a thin pad of alumina (3–4 cm). The eluant was concentrated, and precipitation with pentane gave (η^4-C_4Et_4)Co(CO)$_2$I (**1**) (3.93 g, 9.7 mmol; 45%) as a red-brown solid, m.p. 45–47 °C. Anal. Calc. for ($C_{14}H_{20}O_2ICo$: C, 41.40; H, 4.96; I, 31.25. Found: C, 41.19; H, 4.86; I, 31.60%. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/ether. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.28 (q, 8H, J = 7 Hz, CH$_2$CH$_3$), 1.18 (t, 12H, J = 7 Hz, CH$_2$CH$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 201.6 (CO), 97.6 (C_4Et_4), 19.8 (CH$_2$CH$_3$), 13.7 (CH$_2$CH$_3$); IR: v(CO) 2048, 2008 cm^{-1} (CH$_2$Cl$_2$); v(CO) 2049, 2011 cm^{-1} (KBr).

3.3. Preparation of [(η^6-toluene)(η^4-tetraethylcyclobutadiene)cobalt] hexafluorophosphate (**2**)

[(η^4-C_4Et_4)Co(CO)$_2$I] (2.5 g, 6.16 mmol) and aluminium chloride (8.21 g, 61.6 mmol) were added to dry toluene (30 mL, 282 mmol)

and the solution was heated at reflux overnight. The cooled solution was poured onto ice (40 mL), the aqueous layer was separated, filtered and treated with ammonium hexafluorophosphate (1.004 g, 6.16 mmol). The mixture was stirred at room temperature for 1 h, after which time the yellow precipitate was filtered off, dissolved in acetone and the solution filtered through a short alumina column (3–4 cm). The solution was concentrated to 15–20 mL under reduced pressure, and diethyl ether was added to precipitate [(η^6-C$_6$H$_5$Me)Co(η^4-C$_4$Et$_4$)][PF$_6$] (**2**) (1.88 g, 4.08 mmol; 66%) m.p. 275–280 °C decomp. which was filtered off and air-dried. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/ether. Anal. Calc. for C$_{19}$H$_{28}$F$_6$PCo: C, 49.58; H, 6.13; P, 6.73. Found: C, 49.61; H, 6.08; P, 6.33%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.47–6.29 (m, 5H, C$_6$H$_5$CH$_3$), 2.39 (s, 3H, C$_6$H$_5$CH$_3$), 2.05 (q, 8H, J = 7 Hz, CH$_2$CH$_3$), 1.09 (t, 12H, J = 7 Hz, CH$_2$CH$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 112.0 (toluene *ipso*-C), 99.2, 98.4 (toluene *o*-C, *m*-C), 97.3 (toluene *p*-C), 97.1 (C$_4$Et$_4$), 19.5 (C$_6$H$_5$CH$_3$), 19.1 (CH$_2$CH$_3$), 13.2 (CH$_2$CH$_3$); ^{31}P NMR (121.4 MHz, CDCl$_3$): δ −144.2 (septet, J(P–F) = 713 Hz).

3.4. Preparation of [(η^6-p-xylene)(η^4-tetraethylcyclobutadiene)cobalt] hexafluorophosphate (**3**)

As for **2**, [(η^4-C$_4$Et$_4$)Co(CO)$_2$I] (1.002 g, 2.46 mmol), aluminium chloride (3.28 g, 24.6 mmol), dry *para*-xylene (15 mL, 122 mmol) and ammonium hexafluorophosphate (0.401 g, 2.46 mmol) furnished [(η^6-1,4-C$_6$H$_4$Me$_2$)Co(η^4-C$_4$Et$_4$)][PF$_6$] (**3**) (0.302 g, 0.64 mmol; 26%) m.p. 270–280 °C decomp. as a yellow solid when precipitated from an acetone solution with diethyl ether. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/ether. Anal. Calc. for C$_{20}$H$_{30}$F$_6$PCo: C, 50.64; H, 6.37; Co, 12.42. Found: C, 50.83; H, 6.21; Co, 12.24%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.28 (s, 4H, C$_6$H$_4$(CH$_3$)$_2$), 2.36 (s, 6H, C$_6$H$_4$(CH$_3$)$_2$), 2.01 (q, 8H, J = 8 Hz, CH$_2$CH$_3$), 1.10 (t, 12H, J = 8 Hz, CH$_2$CH$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 110.3 (xylene *ipso*-C), 98.8 (xylene CH), 95.6 (C$_4$Et$_4$), 18.8 (C$_6$H$_4$(CH$_3$)$_2$), 18.7 (CH$_2$CH$_3$), 13.0 (CH$_2$CH$_3$).

3.5. Preparation of [(η^6-mesitylene)(η^4-tetraethylcyclobutadiene)-cobalt] hexafluorophosphate (**4**)

As for **2**, [(η^4-C$_4$Et$_4$)Co(CO)$_2$I] (0.505 g, 1.24 mmol), aluminium chloride (1.65 g, 12.4 mmol), dry mesitylene (15 mL, 108 mmol) and ammonium hexafluorophosphate (0.202 g, 1.24 mmol) furnished [(η^6-1,3,5-C$_6$H$_3$Me$_3$)Co(η^4-C$_4$Et$_4$)][PF$_6$] (**4**) (0.275 g, 0.568 mmol; 45%) m.p. 184–191 °C decomp. as a yellow solid when precipitated from an acetone solution with diethyl ether. Anal. Calc. for C$_{21}$H$_{32}$F$_6$PCo: C, 51.65; H, 6.60; Co 12.07. Found: C, 51.41; H, 6.61; Co 12.10%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.09 (s, 3H, C$_6$H$_3$(CH$_3$)$_3$), 2.32 (s, 9H, C$_6$H$_3$(CH$_3$)$_3$), 1.96 (q, 8H, J = 8 Hz, CH$_2$CH$_3$), 1.08 (t, 12H, J = 8 Hz, CH$_2$CH$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 111.4 (mesitylene *ipso*-C, 98.5 (mesitylene CH)), 94.3 (C$_4$Et$_4$), 18.9 (C$_6$H$_3$(CH$_3$)$_3$), 18.4 (CH$_2$CH$_3$), 13.1 (CH$_2$CH$_3$).

3.6. Preparation of (η^5-formylcyclopentadienyl)(η^4-tetraethylcyclobutadiene)cobalt (**5**) (via Route 2)

[(η^6-C$_6$H$_5$CH$_3$)Co(η^4-C$_4$Et$_4$)][PF$_6$] (0.600 g, 1.3 mmol) in dry acetonitrile (15 mL) was irradiated with UV light for 2 h. In a separate vessel, an excess of sodium was added to freshly cracked cyclopentadiene (1 mL) in dry THF (15 mL) and allowed to react for 1 h. The sodium was removed, ethyl formate (1.4 mL, 17.3 mmol) was added and the reaction was stirred for 1 h at room temperature, and the acetonitrile solution was transferred to it via cannula. The reaction mixture was stirred for a further hour,

passed through a short alumina column, and washed with THF until the eluant ran clear. This was concentrated and chromatographed on alumina (dichloromethane/pentane; 3:1) giving a yellow band that was concentrated under reduced pressure, without heat, to give [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Et$_4$)] (**5**) as a yellow oil (0.294 g, 0.93 mmol; 72%). Anal. Calc. for C$_{18}$H$_{25}$Co: C, 68.35; H, 7.97. Found: C, 68.66; H, 7.94%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.67 (s, C*H*O), 5.19 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 4.97 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 1.92 (q, 8H, J = 7 Hz, C*H*$_2$CH$_3$), 1.04 (t, 12H, J = 7 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 189.6 (*C*HO), 92.6 (C$_5$H$_4$ *ipso*-C), 85.2, 80.5 (C$_5$H$_4$ *C*H,), 83.4 (*C*$_4$Et$_4$), 19.8 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$); IR: ν(HC = O) 1674 cm^{-1} (CH$_2$Cl$_2$).

3.7. Attempted preparation of (η^5-formylcyclopentadienyl)(η^4-tetraethylcyclobutadiene)cobalt (5) via Route 1; formation of (η^5-cyclopentadienyl)(η^4-2,3,4,5-tetraethyl–pyrone)cobalt (18)

Sodium was added to a solution of freshly cracked cyclopentadiene (1 mL) in dry THF (15 mL) and was allowed to react for 1 h. The excess sodium was removed, and ethyl formate (1.4 mL, 18 mmol) was added. The reaction mixture was heated at reflux for 3 h, cooled to room temperature and (η^4-C$_4$Et$_4$)Co (CO)$_2$I, **1**, (0.500 g, 1.23 mmol) was added as a solid. The reaction mixture was stirred overnight, concentrated and chromatographed on alumina (dichloromethane/pentane; 1:2) to give (C$_5$H$_5$)Co(C$_4$Et$_4$CO$_2$) (**18**) (0.02 g, 0.06 mmol; 5 %) m.p. 113–114 °C as the second band; crystals precipitated gradually from a dichloromethane/pentane solution. Anal. Calc. for C$_{18}$H$_{25}$O$_2$Co: C, 65.06; H, 7.58. Found: C, 64.99; H, 7.27. ^{1}H NMR (600 MHz, CDCl$_3$): δ 6.28 (s, 5H, C$_5$*H*$_5$), 3.06 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(5)–C*H*$_2$), 2.80 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(3)–C*H*$_2$), 2.56 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(5)–C*H*$_2$), 2.07 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(4)–C*H*$_2$), 2.04 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(3)–C*H*$_2$), 1.87 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(6)–C*H*$_2$), 1.84 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(4)–C*H*$_2$), 1.65 (dq, 1H, ^2J(H,H) = 14 Hz, ^3J(H,H) = 8 Hz, C(6)–C*H*$_2$), 1.31 (t, 3H, J = 8 Hz, C(5)–CH$_2$C*H*$_3$), 1.27 (t, 3H, J = 8 Hz, C(3)–CH$_2$C*H*$_3$), 1.21 (t, 3H, J = 8 Hz, C(4)–CH$_2$C*H*$_3$), 1.18 (t, 3H, J = 8 Hz, C(6)–CH$_2$C*H*$_3$); ^{13}C NMR (150.8 MHz, CDCl$_3$): δ 174.3 (*C*O$_2$), 102.4 , 97.3, 83.3 and 59.2 (*C*(5), *C*(4), *C*(3), *C*(6)), 82.8 (*C*$_5$H$_5$), 28.5, 25.2, 22.7, 22.6 (C(4)–*C*H$_2$CH$_3$, C(6)–*C*H$_2$CH$_3$, C(5)–*C*H$_2$CH$_3$, C(3)–*C*H$_2$CH$_3$), 16.2, 15.9, 13.7, 11.9 (C(5)–CH$_2$*C*H$_3$, C(3)–CH$_2$*C*H$_3$, C(6)–CH$_2$*C*H$_3$, C(4)–CH$_2$*C*H$_3$); IR: ν(CO) 1703 cm^{-1} (CH$_2$Cl$_2$). The aldehyde complex **5** was eluted as the third band (0.05 g, 0.158 mmol; 13%).

3.8. Preparation of (η^5-formylcyclopentadienyl)(η^4-tetramethylcyclobutadiene)cobalt (7) (via Route 2)

A slurry of [(η^6-C$_6$H$_5$CH$_3$)Co(η^4-C$_4$Me$_4$)][PF$_6$] (0.700 g, 1.73 mmol) in dry acetonitrile was irradiated with UV light for 2 h. It was transferred via cannula to a solution of Na[C$_5$H$_4$CHO] in dry THF (prepared from sodium, freshly cracked cyclopentadiene (2 mL) and ethyl formate (2.8 mL, 34.6 mmol)) and stirred for a further 2 h. The reaction mixture was then concentrated and chromatographed on a silica column; the second fraction to elute (ethyl acetate/dichloromethane; 1:3) precipitated from a pentane/dichloromethane solution to give [(η^5-C$_5$H$_4$CHO)Co (η^4-C$_4$Me$_4$)] (**7**) (0.402 g, 1.54 mmol; 89%) m.p. 114–116 °C as a red-orange solid. Anal. Calc. for C$_{14}$H$_{17}$OCo: C, 64.62; H, 6.58; Co, 22.65. Found: C, 64.14; H, 6.59; Co, 22.14%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.64 (s, 1H, C*H*O), 5.08 (t, 2H, ^3J(H,H) = 2 Hz, C$_5$*H*$_4$), 4.88 (t, 2H, ^3J(H,H) = 2 Hz, C$_5$*H*$_4$), 1.49 (s, 12H, C$_4$*Me*$_4$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 189.7 (*C*HO), 92.8 (C$_5$H$_4$ *ipso*-C), 86.4, 81.0

(C$_5$H$_4$ *C*H), 78.6 (*C*$_4$Me$_4$), 10.6 (C$_4$*Me*$_4$); IR υ/cm^{-1}: ν(C=O) 1670 cm^{-1} (CH$_2$Cl$_2$), 1676 cm^{-1} (KBr).

3.9. Preparation of (η^5-carbomethoxycyclopentadienyl)-(η^4-tetraethylcyclobutadiene)cobalt (6) (via Route 2)

An excess of sodium was added to freshly cracked cyclopentadiene (2 mL) in dry THF (15 ml) and allowed to react for 1 h. The excess sodium was removed, dimethylcarbonate (1.4 mL, 16.6 mmol) was added and the mixture was refluxed for 4 h. In a separate three-necked flask equipped with a condenser, [(η^6-C$_6$H$_5$CH$_3$)Co(η^4-C$_4$Et$_4$)][PF$_6$] (0.600 g, 1.3 mmol) in dry acetonitrile (15 mL), was cooled on ice and irradiated with UV light for 2 hs. The yellow solution turned deep red and was transferred via cannula to the sodium carbomethoxycyclopentadienide solution and stirred at room temperature for 2 h. The reaction mixture was stirred for a further hour, passed through a short alumina column, and washed with THF until the eluant ran clear. The resulting solution was concentrated and chromatographed on alumina (dichloromethane/pentane; 3:1) giving a yellow band that was concentrated under reduced pressure, without heat, to give [(η^5-C$_5$H$_4$CO$_2$Me)Co(η^4-C$_4$Et$_4$)] (**6**) as a yellow oil (0.340 g, 0.98 mmol; 76%). Anal. Calc. for C$_{19}$H$_{27}$O$_2$Co: C, 65.89; H, 7.86. Found: C, 66.00; H, 7.12. ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.20 (m, 2H, C$_5$*H*$_4$), 4.81 (m, 2H, C$_5$*H*$_4$), 3.76 (s, 3H, OC*H*$_3$), 1.94 (q, 8H, J = 7 Hz, C*H*$_2$CH$_3$), 1.06 (t, 12H, J = 7 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 168.5 (*C*O$_2$Me), 83.9 (C$_5$H$_4$ *ipso*-C), 82.9, 81.2 (C$_5$H$_4$ *C*H,), 82.0 (*C*$_4$Et$_4$), 50.8 (O*C*H$_3$), 19.5 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$); IR: ν(CO) 1705 (CH$_2$Cl$_2$).

3.10. Preparation of (η^5-carbomethoxycyclopentadienyl)-(η^4-tetramethylcyclobutadiene)cobalt (8) (via Route 2)

As for **6**, a slurry of [(Me$_4$C$_4$)Co(C$_6$H$_5$CH$_3$)]PF$_6$ (0.800 g, 1.98 mmol) in dry acetonitrile was irradiated with UV light for 2 h. It was transferred via a canula to a solution of Na[C$_5$H$_4$CO$_2$Me] in dry THF (prepared from sodium, freshly cracked cyclopentadiene (2 mL) and dimethyl carbonate (2.8 mL, 33.2 mmol)) and stirred for a further 2 h. The reaction mixture was then concentrated and chromatographed on a silica column. The ester was eluted as the second fraction (an orange band) using ethyl acetate/dichloromethane; 1:9. The product was concentrated and crystals of [(η^5-C$_5$H$_4$CO$_2$Me)Co(η^4-C$_4$Me$_4$)] (**8**) (0.430 g, 1.48 mmol; 75%) m.p. 59–61 °C were precipitated from pentane. Anal. Calc. for C$_{15}$H$_{19}$O$_2$Co: C, 62.07; H, 6.60; Co, 20.30. Found: C, 62.18; H, 6.60; Co, 19.96%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.03 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 4.65 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 3.72 (s, 3H, OC*H*$_3$), 1.41 (s, 12H, C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 168.3 (*C*O$_2$Me), 84.0 (C$_5$H$_4$ *ipso*-C), 84.0, 81.9 (C$_5$H$_4$ *C*H), 76.9 (*C*$_4$Me$_4$), 50.9 (O*Me*), 9.9 (C$_4$*Me*$_4$). IR: ν(C=O) 1701 cm^{-1} (CH$_2$Cl$_2$).

3.11. Preparation of (η^5-hydroxymethylcyclopentadienyl)-(η^4-tetraethylcyclobutadiene) cobalt (9)

A solution of lithium aluminium hydride (1.46 mL, 1.46 mmol) in ether was added with stirring to a solution of [(η^5-C$_5$H$_4$CO$_2$CH$_3$)Co(η^4-C$_4$Et$_4$)], **6**, (0.338 g, 0.98 mmol) in THF (10 mL) at 0 °C. The reaction was stirred overnight, quenched with water (2 mL), extracted with dichloromethane (2 × 10 mL), dried over magnesium sulphate and concentrated. The mixture was chromatographed on alumina (dichloromethane/pentane; 2:1) followed by 100% dichloromethane which elutes the second fraction [(η^5-C$_5$H$_4$CH$_2$OH)Co(η^4-C$_4$Et$_4$)] (**9**) as a low melting solid (0.176 g, 0.55 mmol; 56%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.69 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 4.63 (t, 2H, J = 2 Hz, C$_5$*H*$_4$), 4.34 (d, 2H,

J = 6 Hz, CH$_2$OH), 2.00 (q, 8H, J = 8 Hz, CH$_2$CH$_3$), 1.36 (t, 1H, J = 6 Hz, CH$_2$O*H*) 1.07 (t, 12H, J = 8 Hz, CH$_2$C*H*$_3$).

3.12. Preparation of [(η^5-diethylphosphonatomethylcyclopentadienyl)(η^4-tetraethylcyclobutadiene)cobalt] (**10**)

An excess of sodium was added to a solution of diethylphosphite (0.166 g, 1.2 mmol) in toluene (10 mL) and refluxed for 90 min. The reaction was cooled and the unreacted sodium removed. The solution was reheated to reflux, **9** (0.176 g, 0.55 mmol) was added slowly as a solid, heated at reflux for a further 3 h and then stirred overnight. The reaction was quenched with an aqueous solution of NaHCO$_3$. The organic layer was extracted in toluene, dried over magnesium sulphate, filtered, concentrated and chromatographed on alumina. Using dichloromethane, the first to elute was the unreacted starting alcohol, **9**; a 5% solution of THF in dichloromethane eluted [(η^5-C$_5$H$_4$CH$_2$P(O)(OEt)$_2$)Co(η^4-C$_4$Et$_4$)] (0.140 g, 0.32 mmol; 58% as a red oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.57 (t, 2H, J = 2 Hz, C$_5$H$_4$), 4.36 (t, 2H, J = 2 Hz, C$_5$H$_4$), 4.05 (dq, 4H, ^3J(H,H) = 7 Hz, ^3J(H,P) = 7 Hz, OCH$_2$CH$_3$), 2.83 (d, 2H, ^2J(H,P) = 19 Hz, C$_5$H$_4$C*H*$_2$)), 1.96 (q, 8H, ^3J(H,H) = 7 Hz, C*H*$_2$CH$_3$), 1.29 (t, 6H, ^3J(H,H) = 7 Hz, OCH$_2$C*H*$_3$), 1.06 (t, 12H, ^3J(H,H) = 7 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 85.0 (d, ^2J(C,P) = 4 Hz, C$_5$H$_4$ *ipso*-C), 79.6 (d, ^3J(C,P) = 3 Hz, C$_5$H$_4$ CH,), 78.6 (C$_4$Et$_4$), 78.5 (C$_5$H$_4$ CH,), 61.0 (d, ^2J(C,P) = 7 Hz, OCH$_2$CH$_3$), 25.7 (d, ^1J(C,P) = 139 Hz, C$_5$H$_4$CH$_2$), 18.9 (CH$_2$CH$_3$), 15.5 (OCH$_2$CH$_3$), 13.3 (CH$_2$CH$_3$); ^{31}P NMR (121.4 MHz, CDCl$_3$): δ 26.7.

3.13. Preparation of [(η^5-ferrocenylethenylcyclopentadienyl)-(η^4-tetraethylcyclobutadiene)cobalt] (**11(Z)** and **11(E)**)

n-BuLi in hexanes (0.68 mL, 0.95 mmol) was added dropwise to a cooled solution (−78 °C) of ferrocenylmethyltriphenylphosphonium iodide (0.744 g, 1.27 mmol) in dry THF (20 mL). The mixture was stirred at this temperature for 30 min, and then at room temperature for a further hour. [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Et$_4$)], **5**, (0.200 g, 0.63 mmol) was added as a solid and the mixture stirred overnight. The reaction was quenched with water and the product extracted with dichloromethane. The organic layer was separated, dried over magnesium sulphate, filtered and concentrated. The isomers were isolated by column chromatography on silica (pentane/dichloromethane; 6:1) to give (C$_4$Et$_4$)Co(C$_5$H$_4$–CH=CHFc (**11(Z)**) (0.045 g, 0.09 mmol; 14%) as orange crystals. Anal. Calc. for C$_{29}$H$_{35}$FeCo: C, 69.89; H, 7.08. Found: C, 69.84; H, 7.35%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.03 (d, 1H, ^3J(H,H) = 12 Hz, C*H*=CH), 5.90 (d, 1H, ^3J(H,H) = 12 Hz, CH=C*H*), 4.63 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Co), 4.53 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Co), 4.28 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Fe), 4.08 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Fe), 4.02 (s, 5H, C$_5$*H*$_5$), 1.82 (q, 8H, J = 8 Hz, CH$_2$CH$_3$), 0.81 (t, 12H, J = 8 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 123.2, 122.3, (CH=CH), 91.7 (C$_5$H$_4$ *ipso*-C), 82.3 (C$_5$H$_4$ *ipso*-C), 79.2, 78.6 (C$_5$H$_4$Co CH), 78.8 (C$_4$Et$_4$), 68.3, 66.8 (C$_5$H$_4$Fe CH), 68.1 (C$_5$H$_5$), 18.8 (CH$_2$CH$_3$), 13.2 (CH$_2$CH$_3$); IR: ν(C=C) 1607 cm^{-1} (CH$_2$Cl$_2$), and (C$_4$Et$_4$)Co(C$_5$H$_4$–CH=CHFc (**11(E)**) (0.055 g, 0.11 mmol; 18%) m.p. 43–45 °C. Anal. Calc. for C$_{29}$H$_{35}$FeCo: C, 69.89; H, 7.08. Found: C, 69.98; H, 7.21%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.37 (s, 2H, C*H*=*H*), 4.75 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Co), 4.68 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Co), 4.33 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Fe), 4.19 (t, 2H, J = 2 Hz, C$_5$*H*$_4$Fe), 4.10 (s, 5H, C$_5$*H*$_5$), 1.95 (q, 8H, J = 8 Hz, CH$_2$CH$_3$), 1.06 (t, 12H, J = 8 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 122.8, 122.3, (CH=CH), 94.6 (C$_5$H$_4$ *ipso*-C), 85.4 (C$_5$H$_4$ *ipso*-C), 80.2 (C$_4$Et$_4$), 80.0, 77.5 (C$_5$H$_4$Co CH), 69.0 (C$_5$H$_5$), 68.2, 66.0 (C$_5$H$_4$Fe CH), 20.0 (CH$_2$CH$_3$), 14.4 (CH$_2$CH$_3$); IR: ν(C=C) 1605 cm^{-1} (CH$_2$Cl$_2$), 1638 cm^{-1} (KBr).

3.14. Preparation of [{E-(η^5-{(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt}ethenylcyclopentadienyl)}(η^4-tetraethylcyclobutadiene)cobalt] (**12**)

t-BuLi in pentane (0.32 ml, 0.69 mmol) was added dropwise to a cooled solution (−78 °C) of [(η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$CH$_2$P(O)(OEt)$_2$)] (0.200 g, 0.32 mmol) in dry THF (30 mL). The reaction was stirred at this temperature for 1 h and then allowed to return to room temperature. [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Et$_4$)], **5**, (0.158 g, 0.50 mmol) was added as a solid and the mixture was stirred overnight. The reaction was quenched with water (2 mL), and the organic layer was extracted with dichloromethane, washed with brine, separated, dried over magnesium sulphate, filtered and concentrated. The crude product was chromatographed on silica (pentane gradually changed to pentane/dichloromethane; 2:1). The first product eluted was E-[1,2-[bis(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt]ethene] (0.038 g, 0.04 mmol; 24%). The second band eluted was [(η^4-C$_4$Et$_4$)Co(η^5:η^5-C$_5$H$_4$CH=CHC$_5$H$_4$)Co(η^4-C$_4$Ph$_4$)] (**12(E)**) (0.133 g, 0.17 mmol; 49%) m.p. 115–120 °C. Anal. Calc. for C$_{52}$H$_{50}$Co$_2$·0.5CH$_2$Cl$_2$: C, 75.49; H, 6.15. Found: C, 75.71; H, 6.39%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.42–7.16 (m, 20H, phenyls), 6.05 (d, 1H, ^3J(H,H) = 16 Hz, HC=C*H*), 5.77 (d, 1H, ^3J(H,H) = 16 Hz, *H*C=CH), 4.64 (m, 2H, C$_5$H$_4$), 4.61 (m, 2H, C$_5$H$_4$), 4.60 (m, 2H, C$_5$H$_4$), 4.50 (m, 2H, C$_5$H$_4$), 1.87 (q, 8H, J = 7 Hz, CH$_2$CH$_3$), 0.99 (t, 12H, J = 7 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.3, 127.8, 127.9, 126.0 (C$_4$P*h*$_4$), 124.9, 117.9 (*C*H=CH), 97.4, 94.2 (C$_5$H$_4$ *ipso*-C), 83.7, 80.2, 80.0, 77.7 (C$_5$H$_4$ CH), 80.0, 75.1 (C$_4$Ph$_4$, C$_4$Et$_4$), 19.8 (CH$_2$CH$_3$), 14.2 (CH$_2$CH$_3$). IR: ν(C=C) 1597 cm^{-1} (CH$_2$Cl$_2$).

3.15. Preparation of [{E-(η^5-{(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt}ethenylcyclopentadienyl)}(η^4-tetramethylcyclobutadiene)cobalt] (**13**)

As for **12**, *t*-BuLi in pentane (0.42 ml, 0.5 mmol) was added dropwise to a cooled solution (−78 °C) of [Co(η^4-C$_4$Ph$_4$)(η^5-C$_5$H$_4$CH$_2$P(O)(OEt)$_2$)] (0.315 g, 0.5 mmol) in dry THF (40 ml). The reaction was stirred at this temperature for 1 h and then allowed to return to room temperature. [(η^5-C$_5$H$_4$CHO)Co(η^4-C$_4$Me$_4$)], **7**, (0.130 g, 0.5 mmol) was added as a solid and the mixture was stirred overnight. The reaction was quenched with water (2 ml). The organic layer was extracted with dichloromethane, washed with brine, separated, dried over magnesium sulphate, filtered and concentrated. The crude product was chromatographed on silica (pentane/dichloromethane; 4:3). The first product eluted was E-[1, 2-[bis(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt)] ethene] (0.021 g, 0.02 mmol; 4%). The second band eluted was [(η^4-C$_4$Me$_4$)Co(η^5:η^5-C$_5$H$_4$CH=CHC$_5$H$_4$)Co(η^4-C$_4$Ph$_4$)] (**13(E)**) (0.200 g, 0.27 mmol; 54%), m.p. 150–154 °C. Anal. Calc. for C$_{48}$H$_{42}$Co$_2$: C, 78.26; H, 5.75. Found: C, 77.43; H, 5.78%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.42–7.14 (m, 20H, phenyls), 6.06 (d, 1H, ^3J(H,H) = 16 Hz, C*H*=CH), 5.78 (d, 1H, ^3J(*H*,H) = 16 Hz, CH=C*H*), 4.66 (m, 2H, C$_5$H$_4$), 4.60 (m, 2H, C$_5$H$_4$), 4.51 (m, 2H, C$_5$H$_4$), 4.39 (m, 2H, C$_5$H$_4$), 1.40 (s, 12 H, C*H*$_3$); ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.3, 128.8, 127.9, 126.1 (C$_4$P*h*$_4$), 124.8, 118.1 (CH=CH), 97.5, 94.1 (C$_5$H$_4$ *ipso*-C), 83.8, 80.7, 80.2, 78.1 (C$_5$H$_4$ *C*H), 75.1, 74.8 (C$_4$Ph$_4$, C$_4$Me$_4$), 10.4 (CH$_3$). IR: ν(C=C) 1597 cm^{-1} (CH$_2$Cl$_2$).

3.16. Knoevenagel condensation of (η^5-formylcyclopentadienyl)-(η^4-tetraethylcyclobutadiene)cobalt with malononitrile (**14**)

Two drops of triethylamine were added to a solution of **5** (0.352 g, 1.1 mmol) and malononitrile (0.110 g, 1.7 mmol) in dry

Table 1
Crystallographic data.

	Compound							
	1	**2**	**4**	**6**	**8**	**11(Z)**	**15**	**18**
Empirical formula	$C_{14}H_{20}O_2CoI$	$C_{19}H_{27}CoPF_6$	$C_{21}H_{32}CoPF_6$	$C_{14}H_{17}OCo$	$C_{15}H_{19}O_2Co$	$C_{29}H_{35}FeCo$	$C_{17}H_{17}N_2Co$	$C_{18}H_{25}O_2Co$
fw	406.13	459.31	488.37	260.21	290.23	498.35	308.26	332.31
Crystal system	Monoclinic	Tetragonal	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$I4$ (#79)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	8.8739(7)	8.044(3)	8.6004(13)	7.2629(19)	7.4350(5)	16.035(3)	7.3794(7)	9.7349(8)
b (Å)	13.3915 (10)	8.044(3)	16.305(3)	14.740(4)	8.4817(6)	8.4281(14)	12.6308(13)	14.2700(12)
c (Å)	13.6192(10)	15.778(11)	17.835(3)	11.600(3)	11.5526(8)	35.731(6)	16.1822(16)	12.1581(10)
α (°)	90	90	113.452(2)	90	77.0800(1)	90	90	90
β (°)	104.5240(1)	90	90.188(2)	98.920(4)	83.4260(1)	94.632(3)	91.289(2)	110.2750(1)
γ (°)	90	90	99.632(3)	90	88.8420(1)	90	90	90
V (Å^3)	1566.7(2)	1020.9(9)	2255.2(6)	1226.9(6)	705.40(8)	4813.1(14)	1507.9(3)	1584.3(2)
Z	4	2	4	4	2	8	4	4
D_{calc} (g cm^{-3})	1.722	1.494	1.438	1.409	1.366	1.375	1.358	1.393
T (K)	100(2)	293(2)	100(2)	113(2)	293(2)	100(2)	100(2)	100(2)
Absorption coefficient (mm^{-1})	3.058	0.973	0.885	1.374	1.208	1.306	1.129	1.085
F	800	474	1016	544	304	2096	640	704
θ Range (°)	2.17 to 27.00	2.58 to 28.33	1.25 to 26.00	2.25 to 28.22	1.82 to 28.48	2.05 to 22.00	2.05 to 26.76	2.29 to 27.00
Index ranges	$-11 \leqslant h \leqslant 11$	$-10 \leqslant h \leqslant 10$	$-10 \leqslant h \leqslant 10$	$-9 \leqslant h \leqslant 9$	$-9 \leqslant h \leqslant 9$	$-15 \leqslant h \leqslant 16$	$-9 \leqslant h \leqslant 9$	$-12 \leqslant h \leqslant 12$
	$-17 \leqslant k \leqslant 17$	$-10 \leqslant k \leqslant 10$	$-20 \leqslant k \leqslant 20$	$-18 \leqslant k \leqslant 19$	$-11 \leqslant k \leqslant 11$	$-8 \leqslant k \leqslant 8$	$-15 \leqslant k \leqslant 15$	$-18 \leqslant k \leqslant 18$
	$-17 \leqslant l \leqslant 17$	$-20 \leqslant l \leqslant 20$	$-22 \leqslant l \leqslant 22$	$-15 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 15$	$-37 \leqslant l \leqslant 37$	$-20 \leqslant l \leqslant 20$	$-15 \leqslant l \leqslant 15$
Reflections measured	25 434	7004	34 720	10 218	12 028	16 618	13 473	25 335
Reflections used (R_{int})	3422 (0.0288)	1218 (0.0396)	8864 (0.0421)	2864 (0.0231)	3289 (0.0164)	5855 (0.0797)	3204 (0.0405)	3459 (0.0234)
Parameters	243	85	537	213	239	277	185	290
Final R values $I > 2\sigma(I)$]: R_1, wR_2	0.0178, 0.0428	0.0766, 0.1836	0.0533, 0.1402	0.0282, 0.0693	0.0233, 0.0647	0.0538, 0.1070	0.0548, 0.1331	0.0368, 0.0953
R values (all data): R_1, wR_2	0.0192, 0.0434	0.0775, 0.1847	0.0624, 0.1489	0.0331, 0.0720	0.0239, 0.0652	0.0925, 0.1200	0.0606, 0.1379	0.0387, 0.0965
Goodness-of-fit on F^2	1.115	1.040	1.043	1.075	1.120	0.960	1.073	1.113
Largest diffraction in peak and hole (e Å^{-3})	0.433, −0.300	0.848, −0.483	1.915, −0.400	0.492, −0.249	0.236, −0.398	0.565, −0.449	3.514, −0.251	1.350, −0.265

dichloromethane (30 mL). After 1 h, the solution was concentrated under reduced pressure and the mixture separated by column chromatography on alumina, (pentane/dichloromethane; 3:2). Dark red crystals of $[(C_4Et_4)Co(C_5H_4CH{=}C(CN)_2]$ (**14**) (0.120 g, 0.33 mmol; 30 %) m.p. 48–50 °C. were precipitated from a dichloromethane/pentane mixture. Anal. Calc. for $C_{21}H_{25}N_2Co$: C, 69.22; H, 6.92; N, 7.69; Co, 16.17. Found: C, 68.85; H, 6.75; N, 7.50; Co, 15.70%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 1H, C*H*=C(CN)$_2$), 5.36 (s, 2H, C$_5$*H*$_4$), 5.14 (s, 2H, C$_5$*H*$_4$), 3.82 (q, 8H, J = 7 Hz, C*H*$_2$) 1.06 (t, 12H, J = 7 Hz, C*H*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 158.7 (*C*H=C(CN)$_2$), 115.8, 114.8 (*C*N), 87.7, 82.2 (C$_5$H$_4$ *C*H), 87.3 (C$_5$H$_4$ *ipso*-C), 85.3 (*C*$_4$Et$_4$), 71.2 (*C*(CN)$_2$), 19.7 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$). IR: v(C≡N) 2222, v(C=C) 1568 cm^{-1} (CH$_2$Cl$_2$); v(C≡N) 2218, v(C=C) 1569 cm^{-1} (KBr).

3.17. Knoevenagel condensation of (η^5-formylcyclopentadienyl)-(η^4-tetramethylcyclobutadiene)cobalt with malononitrile (15)

Two drops of triethylamine were added to a solution of **7** (0.040 g, 0.15 mmol) and excess malononitrile (0.015 g, 0.23 mmol) in dry dichloromethane (10 ml). The orange solution immediately changed from orange to dark red. The reaction was stirred for 2 h, concentrated and chromatographed using dichloromethane on a silica column; the product eluted as a red band. Dark red crystals of $[(C_4Me_4)Co(C_5H_4CH{=}C(CN)_2]$ (**15**) (0.042 g, 0.14 mmol; 91%) m.p. 148–151 °C precipitated as a red powder upon concentration under reduced pressure. Anal. Calc. for $C_{17}H_{17}N_2Co$: C, 66.24; H, 5.56; N, 9.09; Co, 19.12. Found: C, 66.54; H, 5.52; N, 8.72; Co. 19.28%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (s, 1H, C*H*=C(CN)$_2$), 5.26 (m, 2H, C$_5$*H*$_4$), 5.05 (m, 2H, C$_5$*H*$_4$), 1.48 (s, 12 H, C*H*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 158.7 (*C*H=C(CN)$_2$), 115.9, 114.9 (*C*≡N), 88.6, 82.6 (C$_5$H$_4$ *C*H), 87.3 (C$_5$H$_4$ *ipso*-C), 80.5 (*C*$_4$Me$_4$), 71.0 (CH=*C*(CN)$_2$), 10.4 (CH$_3$, C$_4$*Me*$_4$). IR: v(C≡N) 2222, v(C=C) 1568 cm^{-1} (CH$_2$Cl$_2$); v(C≡N) 2218, v(C=C) 1570 cm^{-1} (KBr).

3.18. Preparation of [1-((η^5-cyclopentadienyl)(η^4-tetramethyl-cyclobutadiene)cobalt)-2,2-dimethyl-propan-1-ol] (16)

t-BuLi in pentane (0.21 mL, 0.365 mmol) was added to a cooled solution (−78 °C) of **7** (0.100 g, 0.38 mmol) in dry THF (15 ml). The reaction was stirred at this temperature for 30 min before allowing the solution to warm to room temperature. The reaction mixture was stirred overnight, quenched with water (5 ml), extracted with dichloromethane, dried over magnesium sulphate, concentrated and chromatographed on alumina using pentane-dichloromethane; 1:1 to yield $[(C_4Me_4)Co(C_5H_4{-}CH(OH)CMe_3]$ (0.045 g, 0.14 mmol; 37%) as a yellow oil. Anal. Calc. for $C_{18}H_{27}OCo$: C, 67.91; H, 8.55; Co, 18.51. Found: C, 67.57; H, 8.44; Co, 17.84. ^1H NMR (300 MHz, $CDCl_3$): δ 4.54 (m, 1H, C$_5$*H*$_4$), 4.38 (m, 1H, C$_5$*H*$_4$), 4.38 (m, 1H, C$_5$*H*$_4$), 4.37 (m, 1H, C$_5$*H*$_4$), 3.91 (d, 1H, J = 3 Hz, C*H*(OH)), 1.67 (d, 1H, J = 3 Hz, CH(O*H*)) 1.50 (s, 12 H, C$_4$*Me*$_4$), 0.84 (s, 9H, C*Me*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 98.7 (C$_5$H$_4$ *ipso*-C), 78.9, 78.5, 77.4, 75.7 (C$_5$H$_4$) CH), 74.5 (CH(OH)), 72.5 (*C*$_4$Me$_4$), 33.6 (*C*Me$_3$), 24.7 (C*Me*$_3$) 9.4 (C$_4$*Me*$_4$).

3.19. Preparation of [(η^5-cyclopentadienyl)(η^4-tetramethylcyclo-butadiene)cobalt)ferrocenylmethanol] (17)

n-BuLi (0.37 ml, 0.73 mmol) was added to a solution of ferrocenyltributyltin [57] (0.41 g, 0.87 mmol) in dry THF (30 mL) at −78 °C and stirred for 30 min. The solution became orange, and there was also an orange precipitate. To this was added $(C_5H_4CHO)Co(C_4Me_4)$, **7**, (0.150 g, 0.57 mmol) as a solid; the solution turned red and was stirred overnight. The reaction mixture was quenched with water (2 × 10 mL), extracted with CH$_2$Cl$_2$ and

the organic layer was separated, dried over magnesium sulphate, concentrated and chromatographed on an alumina column using pentane/dichloromethane; 1:1) to yield, as the second band, $[(C_4Me_4)Co(C_5H_4{-}CH(OH)Fc]$ (**17**) (0.032 g, 0.07 mmol;13%) as a low-melting solid. ^1H NMR (300 MHz, $CDCl_3$): δ 5.21 (d, 1H, J = 3 Hz, C*H*(OH)), 4.65 (m, 1H, C$_5$*H*$_4$Co), 4.50 (m, 1H, C$_5$*H*$_4$Co), 4.47 (m, 1H, C$_5$*H*$_4$Co), 4.45 (m, 1H, C$_5$*H*$_4$Co), 4.24 (m, 1H, C$_5$*H*$_4$Fe), 4.15 (m, 1H, C$_5$*H*$_4$Fe), 4.12 (m, 1H, C$_5$*H*$_4$Fe), 4.11 (m, 1H, C$_5$*H*$_4$Fe), 4.16 (s, 5H, C$_5$*H*$_5$), 2.16 (s, 1H, J = 3 Hz, CH(O*H*)), 1.58 (s, 12 H, C$_4$*Me*$_4$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 102.1 (C$_5$H$_4$Co *ipso*-C), 93.4 (C$_5$H$_4$Fe *ipso*-C), 80.9, 79.9, 78.5, 77,0 (C$_5$H$_4$Co CH), 74.9 (C$_4$Me$_4$), 68.7 (C$_5$H$_5$), 68.0, 67.9, 67.2, 67.0 (C$_5$H$_4$Fe CH), 67.7 (CH(OH)), 11.6 (C$_4$*Me*$_4$).

3.20. X-ray crystal structure determinations

Crystal data for **1**, **2**, **4**, **7**, **8**, **11(Z)**, **15** and **18** were collected using a Bruker SMART APEX CCD area detector diffractometer and an X-ray tube utilising graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), and are listed in Table 1. A full sphere of reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS [58]. The structures were solved by direct methods using SHELXS-97 [59] and refined by full matrix least-squares on F^2 for all data using SHELXL-97 [60]. For compounds **2**, **4**, **11(Z)** and **15** all hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon/nitrogen atom the H atom is attached to. For compounds **1**, **7**, **8** and **18**, all hydrogen atoms were located in the difference Fourier map and allowed to refine freely with isotropic temperature factors. Anisotropic temperature factors were used for all non-hydrogen atoms.

Appendix A. Supplementary data

CCDC 721142, 721141, 721144, 721146, 721147, 721145, 721148 and 721143 contain the supplementary crystallographic data for **1**, **2**, **4**, **6**, **8**, **11(Z)**, **15** and **18**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.004.

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