

Aldol condensation reactions of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ Christoph Behrendt<sup>a</sup>, Sven Dabek<sup>a</sup>, Jurgen Heck<sup>a,\*</sup>, Donagh Courtney<sup>b</sup>,  
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**Abstract**

The aldol condensation reaction between  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  and a range of aromatic aldehydes  $[\text{RCHO}]$  and  $[\text{RCH}=\text{CH}-\text{CHO}]$  gives a series of  $\alpha,\beta$ -unsaturated ketones  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$  and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{R}\}]$  (**3**). The reaction is promoted by various bases: NaH proved to be the most effective whilst <sup>t</sup>BuLi gave  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{OH})(^t\text{Bu})\text{CH}_3\}]$  as the major product. NaOH was ineffective, perhaps indicating that the methyl protons in  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  are less acidic than those in  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ . Compounds **3** were characterised spectroscopically. Their <sup>1</sup>H NMR spectra are consistent with a *trans* configuration about their C=C bond, and this was confirmed by X-ray crystallography in five cases, which showed that all have the same basic structure with parallel cyclobutadiene and cyclopentadienyl ligands, but they are not identical. The  $\text{C}_5\text{H}_4\text{C}(\text{O})(\text{CH}=\text{CH})_n\text{-R}$  ( $n = 1$  or  $2$ ) moieties show little evidence for delocalisation and often deviate from planarity. The UV/Vis spectra of those **3** with smaller aromatic rings ( $\text{R} = \text{C}_6\text{H}_5$ ,  $4\text{-C}_6\text{H}_4\text{NMe}_2$ ,  $2\text{-C}_4\text{H}_3\text{S}$  and  $1\text{-C}_{10}\text{H}_7$ ) suggest that these are donor- $\pi$ -acceptor systems, but as the annellation of R increases ( $\text{R} = 9\text{-C}_{14}\text{H}_9$ ,  $1\text{-C}_{16}\text{H}_9$  and  $1\text{-C}_{20}\text{H}_{11}$ ) the spectra increasingly resemble those of the parent polycyclic aromatic hydrocarbon, RH. Reduction of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7\text{-1}\}]$  with DIBAL gives a mixture of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{-C}_{10}\text{H}_7\text{-1}\}]$  and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{OH})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7\text{-1}\}]$ . A minor product from the preparation of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  was shown by X-ray crystallography to be the  $\eta^4$ -butadiene complex  $[\text{Co}\{\eta^4\text{-Ph}(\text{H})\text{C}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ .  
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**Keywords:** Cobalt; Tetraphenylcyclobutadiene; Aldol condensation; Unsaturated ketones**1. Introduction**

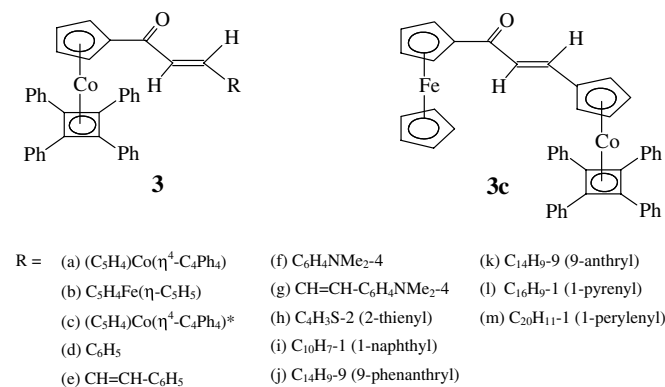
Although the chemistry of ferrocene and its derivatives has been studied extensively, less effort has been expended on their isoelectronic counterparts derived from  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_5)]$ . Here, we report a series of  $\alpha,\beta$ -unsaturated ketones  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$  (Scheme 1) obtained from the base-promoted aldol condensation of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  with various aldehydes RCHO. The reduction of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7\text{-1}\}]$  (**3i**), with DIBAL

has also been studied with the intention of preparing allylic alcohols as precursors to cationic merocyanines such as  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{CHCHCH}-\text{C}_{10}\text{H}_7\text{-1}\}][\text{BF}_4]$ .

Acids and bases promote the reversible formation of aldols from enolisable aldehydes and ketones (Scheme 2, Step 1). The reaction was discovered independently by Borodin [1a] and Wurtz [1b] ca. 1870, and since then it has provided a versatile method for preparing new C—C bonds [1c]. Furthermore, as both of these carbon atoms may end up as chiral centres there has been much recent research into the asymmetric aldol addition reaction [1d]. However, aldols are  $\beta$ -hydroxy-aldehydes or ketones and are, therefore, susceptible to irreversible dehydration with the formation of  $\alpha,\beta$ -unsaturated aldehydes or ketones (Scheme 2, Step 2).

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\* **3c** is  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH=CH-\eta^5-C_5H_4\}Co(\eta^4-C_4Ph_4)]$  (see above).

Scheme 1.

Of particular interest to us is a variant of the aldol condensation in which an aromatic or aliphatic methyl ketone undergoes a base-catalysed condensation with a non-enolisable aromatic aldehyde (Claisen–Schmidt condensation) [1e,1f]. The presence of the adjacent aromatic substituents means that the initially formed aldol dehydrates very readily (Scheme 2, Step 2). In this context the ferrocenyl group is aromatic and the formation of condensation products  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH=CH-R\}]$  from  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH_3\}]$  and  $[RCHO]$  [1g] or  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4CH=CHC(O)R\}]$  from  $[RC(O)CH_3]$  and  $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CHO)]$  [1h] in base-catalysed reactions has been investigated since the earliest days of ferrocene chemistry. Recently, similar aldol condensations of  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH_3\}]$  with  $[4-Et_2NC_6H_4CHO]$  and  $[4-Me_2NC_6H_4CH=CHCHO]$  have been used to prepare  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH=CHC_6H_4NEt_2-4\}]$  and  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH=CH-CH=CHC_6H_4NMe_2-4\}]$ , respectively, which act as calcium ion detectors [1i]. We describe its reaction with  $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$ .

## 2. Experimental

Published procedures were used to prepare  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH_3\}]$  (**1a**) [2],  $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$  (**2a**) [2],  $[Fe(\eta-C_5H_5)\{\eta^5-C_5H_4C(O)CH_3\}]$

(**1b**) [3], and  $[Fe(\eta-C_5H_5)(\eta^5-C_5H_4CHO)]$  (**2b**) [4]. Other chemicals were purchased and used as received.

Unless otherwise stated, all reactions were carried out at room temperature under an atmosphere of nitrogen in dried and deoxygenated solvents. They were monitored by thin-layer chromatography and NMR spectroscopy.

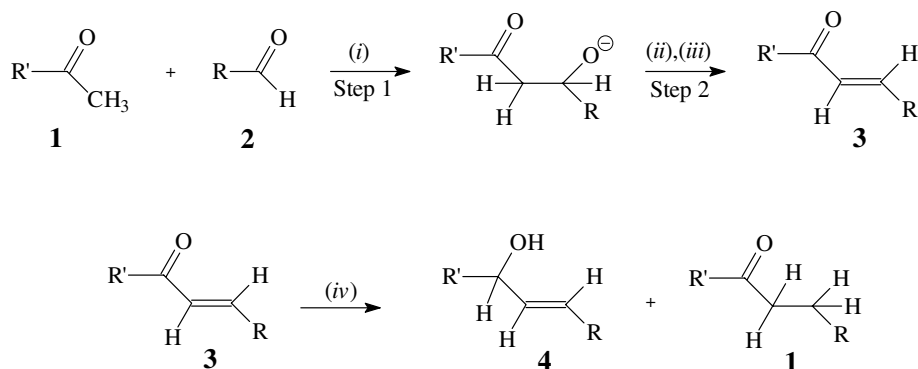
### 2.1. Preparation of $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH_3\}]$ (**1a**), and $[Co\{\eta^4-Ph(H)CC(Ph)C(Ph)CHPh\}\{\eta^5-C_5H_4C(O)CH_3\}]$ (**1c**)

This followed the procedure given in Ref. [2]. A solution of sodium cyclopentadienide from freshly cracked cyclopentadiene (0.5 mL and sodium metal) and methyl acetate (0.61 mL) in tetrahydrofuran (20 mL) was refluxed for 2 h and then cooled. To it was added  $Co(PPh_3)_3Cl$  (5 g), toluene (100 mL) and, after 30 min,  $C_2Ph_2$  (2.0 g). The red mixture was refluxed overnight, cooled, and filtered through Celite. The filtrate was evaporated to dryness, and chromatographed on alumina using toluene–pentane mixtures as eluent. The desired product was the third to be eluted. Concentration of this band at reduced pressure and recrystallization of the residue from dichloromethane–pentane mixtures gave orange-brown crystals of  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH_3\}]$  (**1a**) (yield 0.98 g, 33%).

Further elution gave a deep red band from which was isolated (recrystallisation from dichloromethane/pentane) dark red crystals of  $[Co\{\eta^4-Ph(H)CC(Ph)C(Ph)CHPh\}\{\eta^5-C_5H_4C(O)CH_3\}]$  (**1c**) (yield 0.03 g, 1%).

### 2.2. Aldol condensations using $Li^tBu$ as the deprotonating agent

In a typical reaction, a solution of  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH_3\}]$  (**1b**), (0.197 g, 1 mmol) in dry tetrahydrofuran (15 mL) was cooled to  $-80^\circ C$  and a 2.5 M solution of  $Li^tBu$  in hexane (0.4 mL) added dropwise. The mixture was warmed to  $-60^\circ C$  for 15 min,  $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$  (**2a**), (0.46 g, 1 mmol) added to it and the whole allowed to warm to room temperature. After the addition of water (3 drops) the mixture was allowed to stand for a further hour before the solvent was removed at reduced pressure leaving a red solid. This was extracted



Scheme 2. Conditions: (i) deprotonating agent, (ii)  $+H^+$ , (iii)  $-H_2O$ , (iv) DIBAL.

repeatedly with ether, the ether solution evaporated to dryness, and the residue chromatographed on alumina. Elution with ether–pentane mixtures gave a red band from which could be isolated  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\eta^5\text{-C}_5\text{H}_4\}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$  (**3c**). It was recrystallized from dichloromethane–pentane mixtures as a red solid (yield 15%).

A similar procedure was used for the reaction of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1a**)/Li<sup>*n*</sup>Bu with  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$  (**2b**). On chromatography of the reaction mixture (alumina with 20:80 ethylacetate/pentane) the first compound to be eluted and isolated was  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\eta^5\text{-C}_5\text{H}_4\}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$  (**3b**), as red crystals from dichloromethane–pentane (yield 15%). The second was a brown oily solid from dichloromethane–pentane identified as  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{OH})(^n\text{Bu})(\text{CH}_3)\}]$  (**4a**) (yield 48%).

### 2.3. Aldol condensations using sodium hydride as the deprotonating agent

The procedure adopted was similar to that used for reactions of acetylferrocene but with sodium hydride in place of potassium hydride [5].

#### 2.3.1. Reaction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ (**1b**), with $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$ (**2a**)

Sodium hydride (0.024 g, 1 mmol) was added to a solution of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  in tetrahydrofuran (15 mL). The mixture was allowed to stand for 4 h refluxed for 1 h, cooled to room temperature,  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$  (0.509 g, 1 mmol) added to it, and the whole allowed to stand overnight. Removal of the solvent gave a red residue which was chromatographed on alumina. Elution with ethyl acetate–pentane (20:80) gave a red band from which was isolated red crystals of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\eta^5\text{-C}_5\text{H}_4\}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$  (**3c**), in 55% yield.

Using the same methodology,  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1a**), and various RCHO, **2**, gave the chalcones  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$  (**3**), where R = (a)  $(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ , (b)  $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ , (d)  $\text{C}_6\text{H}_5$ , (e)  $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ , (f)  $\text{C}_6\text{H}_4\text{-NMe}_2\text{-4}$ , (g)  $-\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NMe}_2\text{-4}$ , (h)  $2\text{-C}_4\text{H}_3\text{S}$  (2-thienyl), (i)  $1\text{-C}_{10}\text{H}_7$  (1-naphthyl), (j)  $9\text{-C}_{14}\text{H}_9$  (9-phenanthryl), (k)  $9\text{-C}_{14}\text{H}_9$  (9-anthryl), (l)  $1\text{-C}_{16}\text{H}_9$  (1-pyrenyl), and (m)  $1\text{-C}_{20}\text{H}_{11}$  (1-perylenyl) in fair to good yields.

#### 2.4. Reduction of $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7\text{-1}\}]$

On addition of a 1.5 M solution of diisobutylaluminumhydride, DIBAL, (1.33 mL, 2 mmol) to a solution of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-1\text{-C}_{10}\text{H}_7\}]$  (0.33 g, 0.5 mmol) in toluene (50 mL), the colour turned from orange to deep red. When, after 5 h, methanol was added to the reaction mixture to destroy excess DIBAL, its colour

changed to yellow. Removal of the solvent gave a brown residue, which was chromatographed on alumina. Elution with a 25:75 ethylacetate–pentane mixture gave two bands. From the first was isolated  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{CH}_2-1\text{-C}_{10}\text{H}_7\}$  (yield 22%); from the second  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{OH})\text{CH}=\text{CH}-1\text{-C}_{10}\text{H}_7\}$  (54%). Both were purified by recrystallisation from dichloromethane–pentane.

#### 2.4.1. $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ (**1a**)

Yield 0.98 g, 33%. IR (THF):  $\nu(\text{CO})$ : 1672  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.48–6.98 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 5.20 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.77 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 1.65 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  197.49 (CO), 135.2 (C<sub>ipso</sub>, C<sub>6</sub>H<sub>5</sub>), 128.8, 128.3 (C<sub>ortho</sub> and C<sub>meta</sub>, C<sub>6</sub>H<sub>5</sub>), 127.0 (C<sub>para</sub>, C<sub>6</sub>H<sub>5</sub>), 93.9, 87.7, 83.4 (C<sub>5</sub>H<sub>4</sub>), 76.7 (C<sub>4</sub>Ph<sub>4</sub>), 27.2 (CH<sub>3</sub>). UV/Vis:  $\lambda_{\text{max}}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>): 277, 318 (sh), 412.

#### 2.4.2. $[\text{Co}\{\eta^4\text{-Ph}(\text{H})\text{CC}(\text{Ph})\text{C}(\text{Ph})\text{CHPh}\}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$ (**1c**)

Yield 0.03 g, 1%. Anal. Calc. for C<sub>35</sub>H<sub>29</sub>OCo: C, 80.14; H, 5.57; Co, 11.23. Found: C, 80.30; H, 5.64; Co, 10.75%. IR (KBr):  $\nu(\text{CO})$  1662  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87–6.74 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 4.94 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.21 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 2.16 (s, 3H, CH<sub>3</sub>), 1.61 (s, 2H, CHPh). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$  196.31 (CO), 143.4, 136.9, 129.3, 128.3, 127.2, 125.6 (C<sub>6</sub>H<sub>5</sub>), 98.1 (C=CHPh), 94.9, 90.8 and 84.1 (C<sub>5</sub>H<sub>4</sub>), 54.8 (CHPh) and 27.7 (COCH<sub>3</sub>). UV/Vis:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) (CH<sub>2</sub>Cl<sub>2</sub>): 265 (16442), 411 (638).

#### 2.4.3. $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{CH}_2-\text{C}_{10}\text{H}_7\text{-1}\}]$ (**1d**) (1-C<sub>10</sub>H<sub>7</sub> = 1-naphthyl)

Yield 22%. Mp. 83–86 °C. Anal. Calc. for C<sub>46</sub>H<sub>35</sub>OCo·H<sub>2</sub>O: C, 81.2; H, 5.4; Co, 8.7. Found: C, 81.0; H, 5.4; Co, 8.3%. IR  $\nu/\text{cm}^{-1}$ :  $\nu(\text{CO})$  1662 (KBr). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.0–8.0 [27H, m, C<sub>6</sub>H<sub>5</sub> and 1-C<sub>10</sub>H<sub>7</sub>], 5.20 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)], 4.79 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)], 3.01 [1H, t, J = 8 Hz, CH<sub>2</sub>CH<sub>2</sub>C(O)], 2.48 [1H, t, J = 8 Hz, CH<sub>2</sub>CH<sub>2</sub>C(O)].

#### 2.4.4. $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\eta^5\text{-C}_5\text{H}_4\text{-Co}(\eta^4\text{-C}_4\text{Ph}_4)\}]$ (**3a**)

Yield 40%. Mp. 171–173 °C. Anal. Calc. for C<sub>69</sub>H<sub>50</sub>OCo<sub>2</sub>: C, 81.8; H, 5.0. Found: C, 81.3; H, 5.4%. IR  $\nu/\text{cm}^{-1}$ :  $\nu(\text{CO})$  1652,  $\nu(\text{C}=\text{C})$  1596, 1498 (KBr). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.14–7.38 [40H, m, C<sub>6</sub>H<sub>5</sub>], 6.66 [1H, d, J = 15.4 Hz, CH=CHC(O)], 5.68 [1H, d, J = 15.4 Hz, CH=CHC(O)], 5.10 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)], 4.78 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)], 4.72 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)], 4.65 [2H, Co(η-C<sub>5</sub>H<sub>4</sub>)]. <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  186.5 [CO], 136.8 [CH=CHC(O)], 135.4–126.5 [C<sub>6</sub>H<sub>5</sub>], 122.1 [CH=CHC(O)], 95.4, 92.1, 87.6, 86.2, 83.1 and 82.5 [Co(η-C<sub>5</sub>H<sub>4</sub>)], 76.0 [C<sub>4</sub>Ph<sub>4</sub>]. UV/Vis:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) (CH<sub>2</sub>Cl<sub>2</sub>): 278 (77599), 495 (sh), 402 (sh).

2.4.5.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-\eta^5-C_5H_4\}Fe(\eta^5-C_5H_5)]$  (**3b**)

Yield 15%. Mp. 104–105 °C. Anal. Calc. for  $C_{46}H_{35}OCoFe \cdot CH_3CO_2C_2H_5$ : C, 74.5; H, 5.34; Co, 7.32; Fe, 6.95. Found: C, 73.92; H, 4.92; Co, 7.52; Fe, 7.39%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1647,  $\nu(C=C)$  1589 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.1–7.5 [21H, m,  $C_6H_5$ ,  $CH=CHC(O)$ ], 6.27 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.27 [2H,  $Co(\eta-C_5H_4)$ ], 4.83 [2H,  $Co(\eta-C_5H_4)$ ], 4.39 [2H,  $Fe(\eta-C_5H_4)$ ], 4.31 [2H,  $Fe(\eta-C_5H_4)$ ], 4.09 [5H, s,  $Fe(\eta-C_5H_5)$ ];  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.2 [CO], 142.7 [ $CH=CHC(O)$ ], 135.2, 128.8, 128.1 and 126.8 [ $C_6H_5$ ], 120.4 [ $CH=CHC(O)$ ], 95.2, 87.9 and 83.2 [ $Co(\eta-C_5H_4)$ ], 79.7, 70.8 and 68.8 [ $Fe(\eta-C_5H_4)$ ], 76.7 [ $C_4Ph_4$ ], 69.6 [ $Fe(\eta-C_5H_5)$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 277 (40840), 390 (sh), 491 (620).

2.4.6.  $[Fe(\eta^5-C_5H_5)\{\eta^5-C_5H_4C(O)CH=CH-\eta^5-C_5H_4\}Co(\eta^4-C_4Ph_4)]$  (**3c**)

Yield 55%. Mp. 199–199.5 °C. Anal. Calc. for  $C_{46}H_{35}OCOFe$ : C, 76.9; H, 4.91; Co, 8.20; Fe, 7.77. Found: C, 76.82; H, 5.05; Co, 7.89; Fe, 7.63%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1650 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.4–7.2 [20H, m,  $C_6H_5$ ], 7.17 [1H, d,  $J = 16$  Hz,  $CH=CHCO$ ], 6.34 [1H, d,  $J = 16$  Hz,  $CH=CHCO$ ], 4.93 [2H,  $Co(\eta-C_5H_4)$ ], 4.79 [2H,  $Co(\eta-C_5H_4)$ ], 4.67 [2H,  $Fe(\eta-C_5H_4)$ ], 4.49 [2H,  $Fe(\eta-C_5H_4)$ ], 4.10 [5H, s,  $Fe(\eta-C_5H_5)$ ].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  192.1 [CO], 137.3 [ $RHC=CHCO$ ], 135.4 [ $C_{ipso}$ ,  $C_6H_5$ ], 128.8 and 128.2 [ $C_{ortho}$  and  $C_{meta}$ ,  $C_6H_5$ ], 126.7 ( $C_{para}$ ,  $C_6H_5$ ), 121.9 [ $COCH=CHR$ ], 92.5, 86.7 and 82.6 [ $Co(\eta-C_5H_4)$ ], 80.9, 72.2 and 69.7 [ $Fe(\eta-C_5H_4)$ ], 76.4 [ $Co(\eta-C_4Ph_4)$ ], 69.9 [ $Fe(\eta-C_5H_5)$ ]. UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 359 (5512), 389 (4492), 473 (1837).

2.4.7.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_6H_5\}]$  (**3d**)

Yield 65%. Mp. 173–174 °C. Anal. Calc. for  $C_{42}H_{31}OCo$ : C, 82.48; H, 5.11; Co, 9.64. Found: C, 81.75; H, 5.19; Co, 8.96%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1654,  $\nu(C=C)$  1596 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.1–7.9 (26H, m,  $C_6H_5$ ), 7.29 [d,  $J = 16$  Hz,  $CH=CHC(O)$ ], 6.69 [1H, d,  $J = 16$  Hz,  $CH=CHC(O)$ ], 5.34 [2H,  $Co(\eta-C_5H_4)$ ], 4.86 [2H,  $Co(\eta-C_5H_4)$ ].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.5 [CO], 141.2 [ $CH=CHC(O)$ ], 135.2, 128.8, 128.2 and 126.8 [ $C_6H_5$ ], 123.0 [ $CH=CHC(O)$ ], 95.2, 88.1 and 83.4 [ $Co(\eta-C_5H_4)$ ], 76.9 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 283 (20314), 310 (sh), 405 (2200).

2.4.8.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-CH=CH-C_6H_5\}]$  (**3e**)

Yield 80%. Mp. 188–9 °C. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1645,  $\nu(C=C)$  1595(sh), 1582 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.1–7.6 [25H, m,  $C_6H_5$ ], 7.06 [1H, dd,  $J = 11$  and 15 Hz,  $CH=CHCH=CHC(O)$ ], 6.79 [1H, d,  $J = 15$  Hz,  $CH=CHCH=CHC(O)$ ], 6.51 [1H, dd,  $J = 11$

and 15 Hz,  $CH=CHCH=CHC(O)$ ], 6.07 [1H, d,  $J = 15$  Hz,  $CH=CHCH=CHC(O)$ ], 5.29 [2H,  $Co(\eta-C_5H_4)$ ], 4.83 [2H,  $Co(\eta-C_5H_4)$ ].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  188.0 (CO), 141.0, 140.2, 127.0 and 125.4 [ $CH=CH-CH=CH$ ], 136.6, 135.1, 128.8, 128.3, 128.2, 127.5, 127.0 and 126.8 [ $C_6H_5$ ], 94.9, 88.2 and 83.2 [ $Co(\eta-C_5H_4)$ ], 76.9 [ $C_4Ph_4$ ]. UV/Vis  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 284 (48100), 344 (38100), 407 (sh).

2.4.9.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_6H_4N(CH_3)_2-4\}]$  (**3f**)

Yield 35%. Mp. 180–182 °C. Anal. Calc. for  $C_{46}H_{38}ONCo \cdot CH_3CO_2C_2H_5$ : C, 77.7; H, 6.0; Co, 7.9; N, 1.9. Found: C, 78.2; H, 6.2; Co, 7.4; N, 1.8%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1641,  $\nu(C=C)$  1602, 1576 (KBr).  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  7.0–7.6 [25H, m,  $C_6H_5$ ], ca. 7.20 [ $C_6H_4$ ], ca. 7.20 [ $CH=CHC(O)$ ], 6.64 [1H, d,  $J = 9$  Hz,  $C_6H_4$ ], 6.44 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.31 [2H,  $Co(\eta-C_5H_4)$ ], 4.82 [2H,  $Co(\eta-C_5H_4)$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 263 (63600), 281 (sh), 418 (34000).

2.4.10.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-CH=CH-C_6H_4N(CH_3)_2-4\}]$  (**3g**)

Yield 63%. Mp. 190–191 °C. Anal. Calc. for  $C_{46}H_{38}ONCo$ : C, 81.3; H, 5.6; Co, 8.7; N, 2.1. Found: C, 80.5; H, 5.8; Co, 7.9; N, 1.79%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1642,  $\nu(C=C)$  1602, 1565 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.1–7.6 [25H, m,  $C_6H_5$ ], 7.36 [1H, d,  $J = 9$  Hz,  $C_6H_4$ ], 7.09 [1H, dd,  $J = 11, 15$  Hz,  $CH=CHCH=CHC(O)$ ], 6.74 [1H, d,  $J = 15$  Hz,  $CH=CHCH=CHC(O)$ ], 6.70 [1H, d,  $J = 8$  Hz,  $C_6H_4$ ], 6.34 [1H, dd,  $J = 11, 15.3$  Hz,  $CH=CHCH=CHC(O)$ ], 5.98 [1H, d,  $J = 15$  Hz,  $CH=CHCH=CHC(O)$ ], 5.27 [2H,  $Co(\eta-C_5H_4)$ ], 4.80 [2H,  $Co(\eta-C_5H_4)$ ], 3.02 [6H, s,  $N(CH_3)_2$ ].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.5 (CO), 142.4, 141.2, 124.2 and 123.2 [ $CH=CH-CH=CH$ ], 150.2, 135.2, 128.8, 128.5, 128.1, 126.7 and 124.8 [ $C_6H_5$ ,  $C_6H_4$ ], 95.6, 87.8 and 83.1 [ $Co(\eta-C_5H_4)$ ], 76.7 [ $C_4Ph_4$ ], 40.3 [ $N(CH_3)_2$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 281 (49100), 431 (39900).

2.4.11.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_4H_3S-2\}]$  (**3h**)

Yield 26%. Mp. 183–184 °C. Anal. Calc. for  $C_{40}H_{29}OSCo$ : C, 77.91; H, 4.74; Co, 9.56; S, 5.19. Found: C, 77.65; H, 4.85; Co, 9.52; S, 5.23%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1647,  $\nu(C=C)$  1586 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.0–7.6 [23H, m,  $C_6H_5$ , and  $C_4H_3S$ ], ca. 7.4 [ $CH=CHC(O)$ ], 6.53 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.41 [2H, t,  $Co(\eta-C_5H_4)$ ], 4.95 [2H, t,  $Co(\eta-C_5H_4)$ ].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.2 [CO], 140.9 [ $CH=CHC(O)$ ], 135.0, 128.8, 128.2 and 126.8 [ $C_6H_5$ ], 133.8, 131.1, 128.3, [ $C_4H_3S$ ] 121.9 [ $CH=CHC(O)$ ], 95.2, 88.1 and 83.4 [ $Co(\eta-C_5H_4)$ ], 76.9 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 278 (79000), 341 (17000), 408 (sh).



2.4.12.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_{10}H_7-1\}]$   
(**3i**) ( $1-C_{10}H_7 = 1$ -naphthyl)

Yield 75%. Mp. 209–210 °C. Anal. Calc. for  $C_{46}H_{33}OCo \cdot H_2O$ : C, 81.4; H, 5.2; Co, 8.7. Found: C, 81.0; H, 5.4; Co, 8.3%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1647,  $\nu(C=C)$  1595 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.0–8.1 [27H, m,  $C_6H_5$  and  $1-C_{10}H_7$ ], 8.19 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 6.80 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.38 [2H, Co( $\eta$ - $C_5H_4$ )], 4.86 [2H, Co( $\eta$ - $C_5H_4$ )].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.4 [CO], 138.0 [ $CH=CHC(O)$ ], 135.1–124.8 [ $C_6H_5$  and  $C_{10}H_7$ ], 123.9 [ $CH=CHC(O)$ ], 95.2, 88.3 and 83.5 [Co( $\eta$ - $C_5H_4$ )], 77.0 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 257 (47400), 278 (44400), 347 (20800), 421(sh).

2.4.13.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_{14}H_9-9\}]$   
(**3j**) ( $9-C_{14}H_9 = 9$ -phenanthryl)

Yield 35%. Mp. 244–246 °C. Anal. Calc. for  $C_{50}H_{34}OCo \cdot CH_3CO_2C_2H_5$ : C, 81.2; H, 5.3; Co, 7.4. Found: C, 81.4; H, 5.2; Co, 7.6%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1651,  $\nu(C=C)$  1598, 1498 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.19 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 7.64–8.75 [9H, m,  $9-C_{14}H_9$ ], 7.15–7.47 [20H, m,  $C_6H_5$ ], 6.77 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.42 [2H, Co( $\eta$ - $C_5H_4$ )], 4.90 [2H, Co( $\eta$ - $C_5H_4$ )].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.5 [CO], 138.5 [ $CH=CHC(O)$ ], 135.2–122.5 [ $C_6H_5$  and  $C_{20}H_{11}$ ], 124.8 [ $CH=CHC(O)$ ], 95.0, 88.2 and 83.5 [Co( $\eta$ - $C_5H_4$ )], 76.9 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 256 (96716), 274 (85636), 350 (24541).

2.4.14.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_{14}H_9-9\}]$   
(**3k**) ( $9-C_{14}H_9 = 9$ -anthryl)

Yield 50%. Mp. 209–210 °C. Anal. Calc. for  $C_{50}H_{35}OCo$ : C, 84.5; H, 4.9; Co, 8.3. Found: C, 82.05; H, 5.22; Co, 8.34%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1651,  $\nu(C=C)$  1592 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.0–8.1 [27H, m,  $C_6H_5$  and  $1-C_{14}H_9$ ], 8.44 [1H, s,  $C_{14}H_9$ ], 8.41 [1H, d,  $J = 16$  Hz,  $CH=CHC(O)$ ], 6.64 [1H, d,  $J = 16$  Hz,  $CH=CHC(O)$ ], 5.31 [2H, Co( $\eta$ - $C_5H_4$ )], 4.89 [2H, Co( $\eta$ - $C_5H_4$ )]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 254 (120000), 280 (sh), 410 (16400, br).

2.4.15.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_{16}H_9-1\}]$   
(**3l**) ( $1-C_{16}H_9 = 1$ -pyrenyl)

Yield 55%. Mp. 187–188 °C. Anal. Calc. for  $C_{52}H_{35}OCo \cdot 1/2CH_2Cl_2$ : C, 81.1; H, 4.6; Co, 7.6. Found: C, 81.9; H, 5.07; Co, 7.43%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1646,  $\nu(C=C)$  1596, 1578 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.46 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 7.8–8.45 [9H, m,  $1-C_{16}H_9$ ], 7.0–7.6 [20H, m,  $C_6H_5$ ], 6.90 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.44 [2H, Co( $\eta$ - $C_5H_4$ )], 4.91 [2H, Co( $\eta$ - $C_5H_4$ )].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.4 [CO], 137.8 [ $CH=CHC(O)$ ], 135.1–124.3 [ $C_6H_5$  and  $C_{16}H_9$ ], 123.1 [ $CH=CHC(O)$ ], 95.4, 88.2 and 83.5 [Co( $\eta$ - $C_5H_4$ )], 77.0 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 266 (44700), 287 (44900), 389 (25800), 419 (26100).

2.4.16.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH=CH-C_{20}H_{11}-1\}]$   
(**3m**) ( $1-C_{20}H_{11} = 1$ -perylene)

Yield 65%. Mp. 243–245 °C. Anal. Calc. for  $C_{56}H_{37}OCo \cdot 1/2CH_2Cl_2$ : C, 82.1; H, 4.6. Found: C, 82.3; H, 5.9%. IR  $\nu/cm^{-1}$ :  $\nu(CO)$  1644,  $\nu(C=C)$  1587, 1498 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.13 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 7.39–8.29 [11H, m,  $3-C_{20}H_{11}$ ], 7.17–7.26 [20H, m,  $C_6H_5$ ], 6.73 [1H, d,  $J = 15$  Hz,  $CH=CHC(O)$ ], 5.40 [2H, Co( $\eta$ - $C_5H_4$ )], 4.90 [2H, Co( $\eta$ - $C_5H_4$ )].  $^{13}C$  NMR (75.4 MHz,  $CDCl_3$ ):  $\delta$  187.5 [CO], 137.5 [ $CH=CHC(O)$ ], 135.2–119.8 [ $C_6H_5$  and  $C_{20}H_{11}$ ], 124.0 [ $CH=CHC(O)$ ], 88.2 and 83.5 [Co( $\eta$ - $C_5H_4$ )], 77.0 [ $C_4Ph_4$ ]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 258 (65026), 288 (44205), 470 (30667).

2.4.17.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(OH)(C_4H_9)CH_3\}]$   
(**4a**)

Yield 50%. Red-brown oil. Anal. Calc. for  $C_{39}H_{27}OCo \cdot CH_2Cl_2$ : C, 73.3; H, 4.43; Co, 9.0. Found: C, 73.06; H, 5.90; Co, 8.93%. IR  $\nu/cm^{-1}$ :  $\nu(OH)$  3550 ( $CH_2Cl_2$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.6–7.0 [20H, m,  $C_6H_5$ ], 4.96 [1H, m, Co( $\eta$ - $C_5H_4$ )], 4.82 [1H, Co( $\eta$ - $C_5H_4$ )], 4.51 [1H, Co( $\eta$ - $C_5H_4$ )], 4.43 [1H, m, Co( $\eta$ - $C_5H_4$ )], 1.4 [2H, m,  $CH_2CH_2CH_2CH_3$ ], 1.1 [1H, s, OH], 1.08–1.02 [4H, m,  $CH_2CH_2CH_2CH_3$ ], 1.13 [3H, s,  $CH_3$ ], 0.77 [3H, t,  $J = 6.8$  Hz,  $CH_2CH_2CH_2CH_3$ ].  $^{13}C$  NMR (125.7 MHz,  $CDCl_3$ ):  $\delta$  136.8, 129.1, 128.5 and 126.6 [ $C_6H_5$ ], 111.1, 83.3, 83.1, 81.1 and 80.2 [Co( $\eta$ - $C_5H_4$ )], 75.2 [ $C_4Ph_4$ ], 71.8 [ $C(OH)$ ], 44.3, 27.8, 26.5, 23.2 14.3 [ $C(OH)(CH_3)CH_2CH_2CH_2CH_3$ ].

2.4.18.  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4CH(OH)CH=CH-C_{10}H_7-1\}]$   
(**4b**) ( $1-C_{10}H_6 = 1$ -naphthyl)

Yield 55%. Mp. 87–90 °C. Anal. Calc. for  $C_{46}H_{35}OCo \cdot 1/2CH_2Cl_2$ : C, 77.8; H, 5.4; Co, 7.8. Found: C, 79.0; H, 5.1; Co, 7.75%. IR  $\nu/cm^{-1}$ :  $\nu(OH)$  3436 (KBr).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.1–8.0 [27H, m,  $C_6H_5$  and  $1-C_{10}H_7$ ], 7.08 [1H, d,  $J = 16$  Hz,  $CH=CHC(OH)$ ], 6.10 [1H, dd,  $J = 6, 16$  Hz,  $CH=CHC(O)$ ], 4.92 [2H, Co( $\eta$ - $C_5H_4$ ) and  $CH(OH)$ ], 4.74 [1H, Co( $\eta$ - $C_5H_4$ )], 4.64 [1H, Co( $\eta$ - $C_5H_4$ )], 4.59 [1H, Co( $\eta$ - $C_5H_4$ )], 1.6 [1H, OH]. UV/Vis:  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 263 (41900), 296 (44800), 408 (1900).

## 2.5. Crystal structure determination

Crystals of **1c**, **3e**, **3g**, **3i** and **3k** were grown from dichloromethane–pentane mixtures and of **3d** and **3h** from toluene–hexane mixtures. Data were collected on a Bruker SMART Apex CCD diffractometer controlled by SMART [6], processed using SAINT [7] and semi-empirical absorption corrections based on redundant reflections applied using SADABS [8]. The structure was solved using SHELXS-97 [9] and refined by full-matrix least-squares on  $F^2$  using SHELXL-97 [10]. All non-hydrogen atoms were assigned anisotropic temperature factors. The hydrogen atoms of **3d**, **3e**, **3g** and **3i** were refined as were the terminal H atoms,

Table 1  
Crystal data for  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH-R}\}]$  complexes

R	$\text{C}_6\text{H}_5$ ( <b>3d</b> )	$\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ ( <b>3e</b> )	$\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NMe}_2\cdot 4$ ( <b>3g</b> )	$2\text{-C}_4\text{H}_3\text{S}$ ( <b>3h</b> )	$1\text{-C}_{10}\text{H}_7$ ( <b>3i</b> )	$9\text{-C}_{14}\text{H}_9$ ( <b>3k</b> )	<b>1c<sup>a</sup></b>
Empirical formula	$\text{C}_{42}\text{H}_{31}\text{OCo}$	$\text{C}_{44}\text{H}_{33}\text{OCo}$	$\text{C}_{46}\text{H}_{38}\text{NOCo}$	$\text{C}_{40}\text{H}_{29}\text{OSCo}$	$\text{C}_{46}\text{H}_{33}\text{OCo}$	$\text{C}_{50}\text{H}_{35}\text{OCo}$	$\text{C}_{35}\text{H}_{29}\text{OCo}$
Formula weight	610.60	636.63	679.70	616.62	660.65	710.71	524.51
<i>T</i> (K)	100(2)	100(2)	100(2)	293(2)	100(2)	100(2)	100(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub> (#33)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>Pna</i> 2 <sub>1</sub> (#33)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>Aba</i> 2 (#41)
Unit cell dimensions							
<i>a</i> (Å)	17.4395(16)	16.4586(14)	24.549(5)	17.6869(18)	10.770(2)	16.186(2)	13.4856(16)
<i>b</i> (Å)	12.4667(12)	12.3073(10)	9.8275(19)	12.5070(13)	17.396(3)	9.1822(12)	21.449(3)
<i>c</i> (Å)	27.938(3)	16.8219(14)	14.089(3)	27.912(3)	17.358(3)	24.669(3)	18.287(2)
$\alpha$ (°)	90	90	90	90	90	90	90
$\beta$ (°)	90	112.200(1)	90.789(3)	90	96.960(3)	106.750(2)	90
$\gamma$ (°)	90	90	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	6074.0(10)	3154.9(5)	3398.6(11)	6174.3(11)	3228.2(11)	3510.9(8)	5289.4(11)
<i>Z</i>	8	4	4	8	4	4	8
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.335	1.340	1.328	1.327	1.359	1.345	1.317
Absorption coefficient (mm <sup>-1</sup> )	0.599	0.579	0.543	0.655 mm <sup>-1</sup>	0.569	0.529 mm <sup>-1</sup>	0.675
<i>F</i> (000)	2544	1328	1424	2560	1376	1480	2192
Crystal size (mm <sup>3</sup> )	1.00 × 1.00 × 0.50	0.30 × 0.20 × 0.20	0.40 × 0.40 × 0.05	0.50 × 0.50 × 0.50	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.10	1.00 × 0.60 × 0.50
$\theta$ Range for data collection (°)	1.46–28.30	2.11–27.00	1.66–26.00	1.78–26.00	1.66–27.00	1.35–24.00	1.90–28.28
Index ranges	–23 ≤ <i>h</i> ≤ 23, –16 ≤ <i>k</i> ≤ 16, –37 ≤ <i>l</i> ≤ 36	–20 ≤ <i>h</i> ≤ 20, –15 ≤ <i>k</i> ≤ 15, –21 ≤ <i>l</i> ≤ 21	–30 ≤ <i>h</i> ≤ 30, –12 ≤ <i>k</i> ≤ 12, –17 ≤ <i>l</i> ≤ 17	–20 ≤ <i>h</i> ≤ 21, –15 ≤ <i>k</i> ≤ 15, –24 ≤ <i>l</i> ≤ 34	–13 ≤ <i>h</i> ≤ 13, –22 ≤ <i>k</i> ≤ 22, –22 ≤ <i>l</i> ≤ 22	–18 ≤ <i>h</i> ≤ 18, –10 ≤ <i>k</i> ≤ 10, –28 ≤ <i>l</i> ≤ 28	–17 ≤ <i>h</i> ≤ 17, –26 ≤ <i>k</i> ≤ 27, –23 ≤ <i>l</i> ≤ 23
Reflections collected	97767	25659	50459	31710	53083	43112	21934
Independent reflections ( <i>R</i> <sub>int</sub> )	14519 (0.0401)	6879 (0.0361)	6687 (0.0356)	10517 (0.0325)	7039 (0.0293)	5520 (0.0828)	6180 (0.0169)
Completeness to $\theta = 26.00^\circ$ (%)	98.0	99.9	100.0	99.9	100.0	100.0	97.0
Absorption correction		Semi-empirical from equivalents	Semi-empirical from equivalents	Numerical	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	0.7540 and 0.5859	0.8929 and 0.7052	0.9734 and 0.7568	0.7355 and 0.7355	0.8947 and 0.7384	0.9490 and 0.5525	0.7289 and 0.5602
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	14519/1/1042	6879/0/547	6687/0/594	10517/1/777	7039/0/565	5520/0/469	6180/1/343
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.024	1.084	1.043	1.051	1.285	1.024
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0364, <i>wR</i> <sub>2</sub> = 0.0884	<i>R</i> <sub>1</sub> = 0.0398, <i>wR</i> <sub>2</sub> = 0.0914	<i>R</i> <sub>1</sub> = 0.0395, <i>wR</i> <sub>2</sub> = 0.0990	<i>R</i> <sub>1</sub> = 0.0445, <i>wR</i> <sub>2</sub> = 0.1119	<i>R</i> <sub>1</sub> = 0.0385, <i>wR</i> <sub>2</sub> = 0.0961	<i>R</i> <sub>1</sub> = 0.0742, <i>wR</i> <sub>2</sub> = 0.1510	<i>R</i> <sub>1</sub> = 0.0287, <i>wR</i> <sub>2</sub> = 0.0736
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0407, <i>wR</i> <sub>2</sub> = 0.0908	<i>R</i> <sub>1</sub> = 0.0542, <i>wR</i> <sub>2</sub> = 0.0988	<i>R</i> <sub>1</sub> = 0.0449, <i>wR</i> <sub>2</sub> = 0.1026	<i>R</i> <sub>1</sub> = 0.0504, <i>wR</i> <sub>2</sub> = 0.1170	<i>R</i> <sub>1</sub> = 0.0417, <i>wR</i> <sub>2</sub> = 0.0986	<i>R</i> <sub>1</sub> = 0.0824, <i>wR</i> <sub>2</sub> = 0.1544	<i>R</i> <sub>1</sub> = 0.0296, <i>wR</i> <sub>2</sub> = 0.0743
Absolute structure parameter	0.079(7)			0.117(13)			–0.004(8)
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.394 and –0.223	0.623 and –0.219	0.697 and –0.274	1.015 and –0.204	0.558 and –0.167	0.823 and –0.759	0.386 and –0.196

<sup>a</sup>  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4\text{H}_2)\{\eta\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Me}\}]$ .

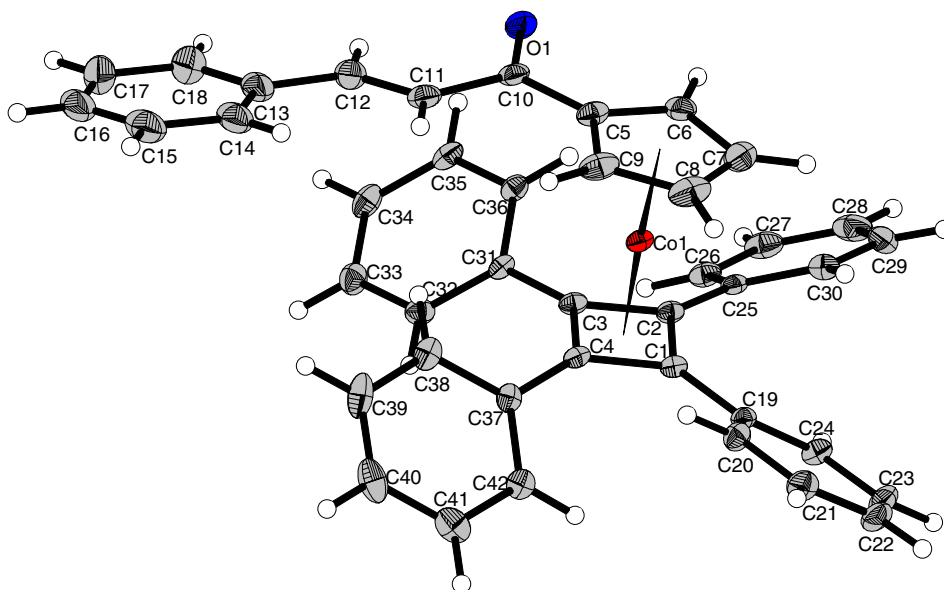


Fig. 1. The structure of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{C}_6\text{H}_5\}]$  (**3d**); thermal ellipsoids are drawn at the 50% probability level.

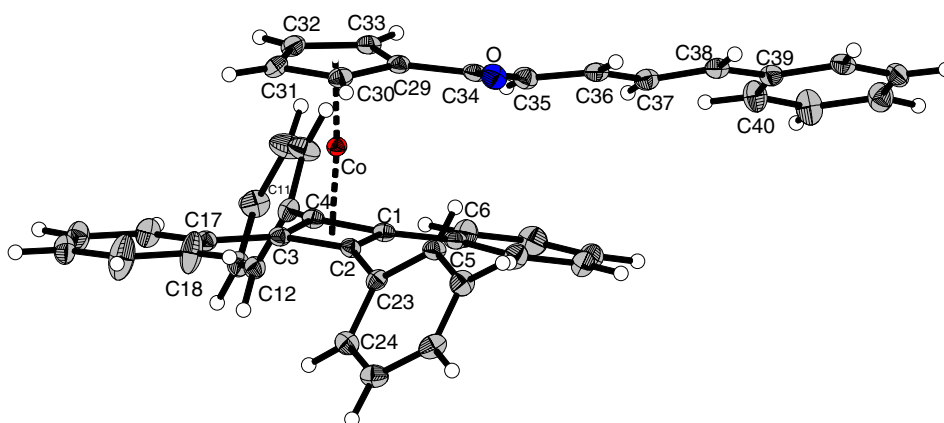


Fig. 2. The structure of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5\}]$  (**3e**); thermal ellipsoids are drawn at the 50% probability level.

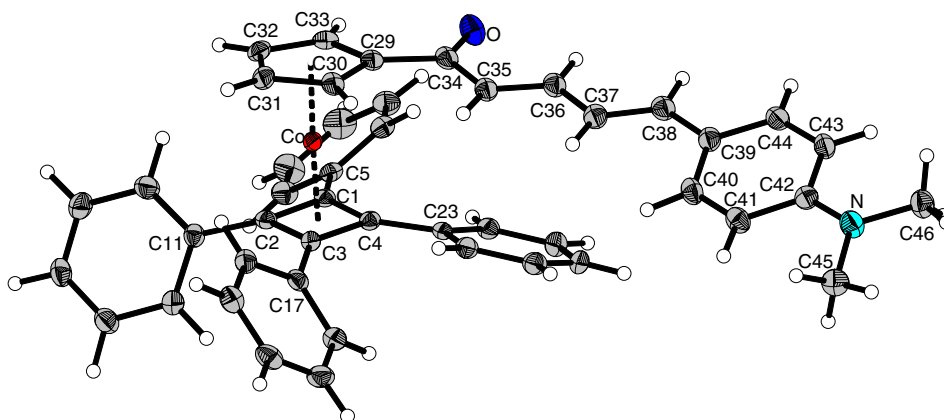


Fig. 3. The structure of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NMe}_2\}]$  (**3g**); thermal ellipsoids are drawn at the 50% probability level.

on C(1) and C(4), of **1c**. The H atoms of **3h**, **3i** and the remainder of those of **1c** were included in calculated positions and refined using a riding model.

Crystal data are summarised in Table 1, and molecular structures and atom labelling are illustrated in Figs. 1–7.

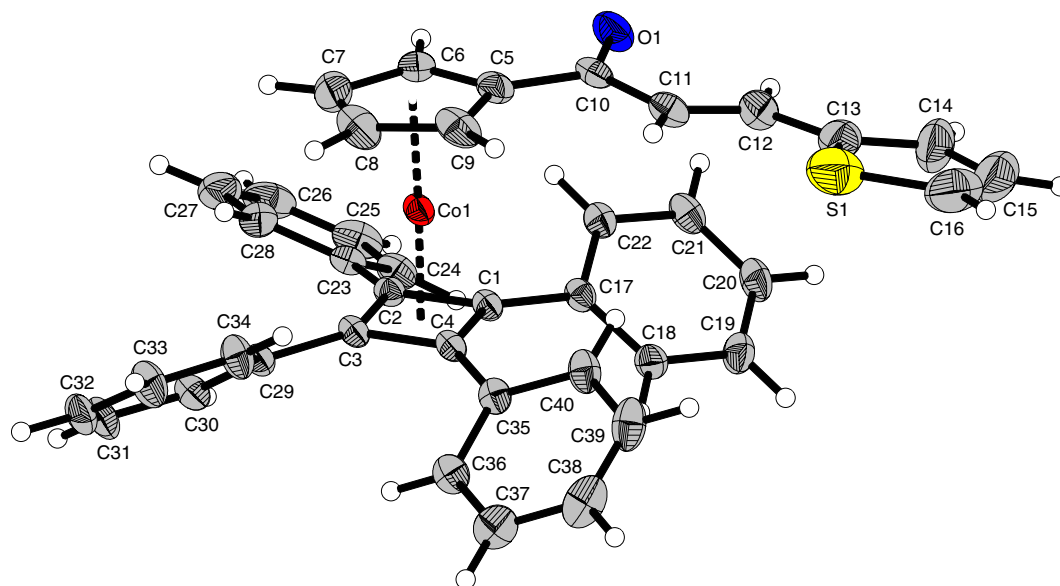


Fig. 4. The structure of  $[\text{Co}(\eta^4\text{-C}_6\text{H}_5)_4\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}\text{-C}_4\text{H}_3\text{S}\}]$  (**3h**) (molecule 1); thermal ellipsoids are drawn at the 25% probability level.

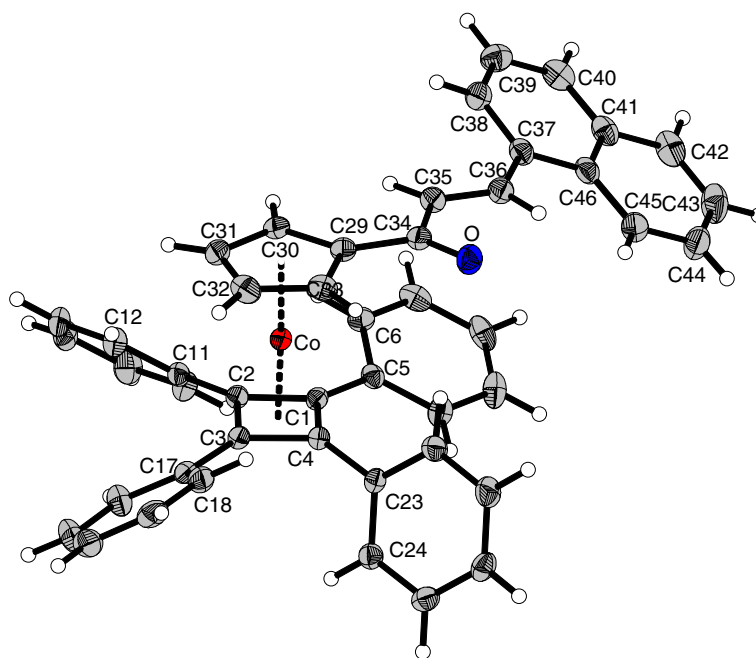


Fig. 5. The structure of  $[\text{Co}(\eta^4\text{-C}_6\text{H}_5)_4\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}\text{-C}_{10}\text{H}_7\text{-1}\}]$  (**3i**); thermal ellipsoids are drawn at the 50% probability level.

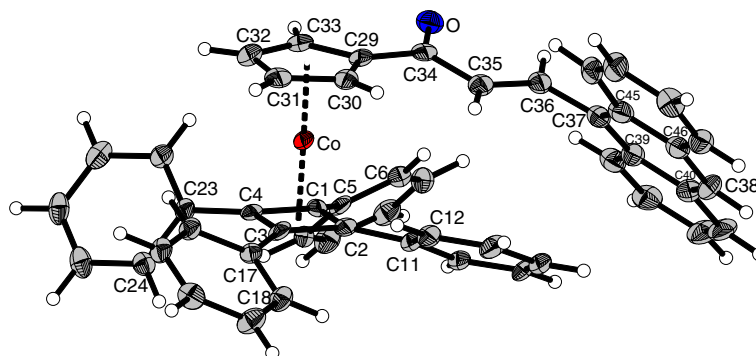


Fig. 6. The structure of  $[\text{Co}(\eta^4\text{-C}_6\text{H}_5)_4\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}\text{-C}_{14}\text{H}_9\text{-9}\}]$  (**3k**); thermal ellipsoids are drawn at the 50% probability level.



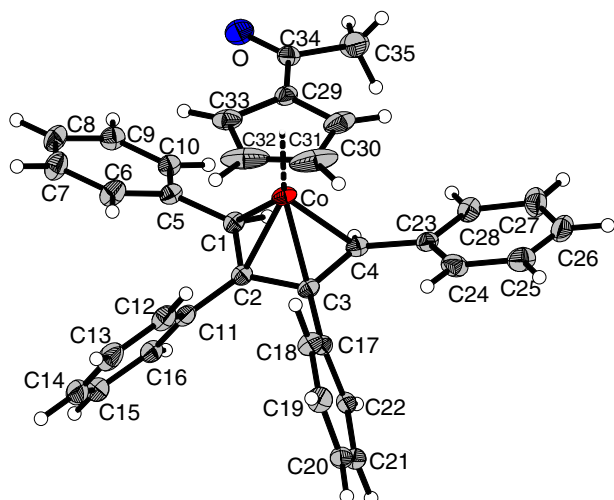


Fig. 7. The structure of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4\text{H}_2)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1c**); thermal ellipsoids are drawn at the 50% probability level.

### 3. Results and discussion

The reactions investigated in the course of this work are summarised in Scheme 1. They are the base-promoted reaction of methyl ketones **1** with aldehydes **2** (the Claisen–Schmidt variant of the aldol condensation reaction). The initially formed aldols undergo facile dehydration to  $\alpha,\beta$ -unsaturated ketones **3** (e.g., Scheme 2). Compounds **3** are reduced to a mixture of saturated ketones **1** and allylic alcohols **4**.

We wished to use  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1a**) as the ketone but, unlike ferrocene,  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_5)]$  does not readily undergo a Friedel–Crafts acylation on the five-membered ring to give  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  [**11**]. However, there is a well-established route to this compound [**2**] using pre-formed sodium acetylcyclopentadienide as outlined in Scheme 3 and described in Section 2.

In our hands this not only gave  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1a**), in modest yield, but it also gave a second  $\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3$  complex in very low yields of ca. 1% which X-ray diffraction showed to be  $[\text{Co}\{\eta^4\text{-Ph}(\text{H})\text{CC}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{H})\text{Ph}\}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  (**1c**), with an  $\eta^4\text{-cis-1,2,3,4}$ -tetraphenylbuta-1,3-diene ligand. It is further discussed below.

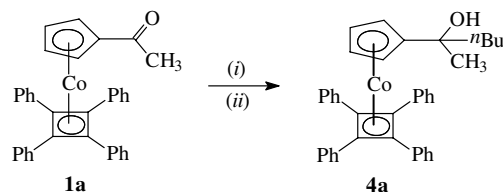
NaOH in aqueous ethanol failed to bring about the reaction of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  with vari-

ous aromatic aldehydes, and although  $\text{Li}^n\text{Bu}$  deprotonated both  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  to their respective enolate anions, it proved to be unsatisfactory. Yields of the desired products from aldol condensation reactions were low due, in part at least, to the competing reaction involving nucleophilic attack by a butyl anion on the acetyl carbonyl group to give tertiary alcohol **4a** (Scheme 4).

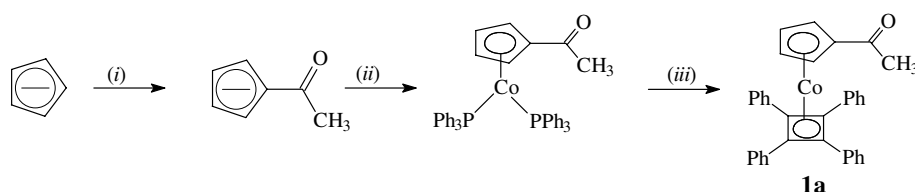
Consequently, we used an alkali metal hydride as the deprotonating agent as described by Floriani et al. [**5**]. They showed that KH promoted the aldol condensation between  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  and  $[\text{RCHO}]$ , and we found that NaH promoted similar condensations of both  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  with a range of aldehydes to give  $\alpha,\beta$ -unsaturated ketones, normally in good yields and without side-products. We assume that the hydride anion deprotonates the acetylcyclopentadienyl complexes to their enolate anions which are the active species (Scheme 5).

#### 3.1. Spectra

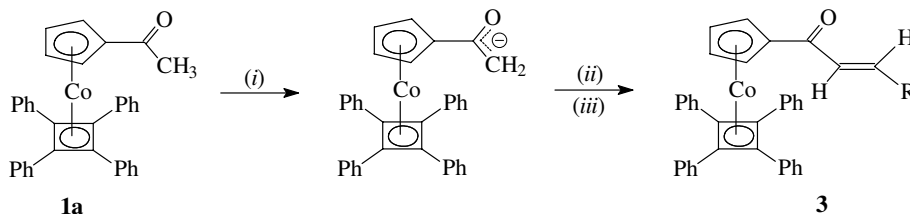
The IR spectra of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$ ,  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  and  $[(\eta^4\text{-C}_4\text{Ph}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})\text{CH}_2\text{CH}_2(\text{C}_{10}\text{H}_7\text{-1})]$  (**1d**), the saturated counterpart of **3i**, between 1500 and 1700  $\text{cm}^{-1}$  each show a strong absorption band together with a number of weak bands. The strong bands are found at 1683, 1672 and 1662  $\text{cm}^{-1}$ , respectively, and are assigned to  $\nu(\text{CO})$  vibrations. They are normal for aromatic aldehydes and ketones (cf. 1684  $\text{cm}^{-1}$  for  $\text{C}_6\text{H}_5\text{CHO}$ ). In the corresponding regions of the spectra of **3a–d**, **3f** and **3g–m** there are normally two bands of comparable intensities at 1646–1654 and 1579–1596  $\text{cm}^{-1}$  which are attributed to the  $\nu(\text{CO})$  and  $\nu(\text{C}=\text{C})$  modes of the  $\text{C}(\text{=O})\text{CH}=\text{CH}$ - moieties. There are other weak bands in the same region that are probably due to the internal vibrations of the various end-groups.



Scheme 4. Conditions: (i)  $n\text{BuLi}$ ; (ii)  $\text{H}_2\text{O}$ .



Scheme 3. Conditions: (i)  $[\text{MeCO}_2\text{Me}]$ ; (ii)  $[\text{Co}(\text{PPh}_3)_3\text{Cl}]$ ; (iii)  $[\text{C}_2\text{Ph}_2]$ ,  $\Delta$ .

Scheme 5. Conditions: (i) NaH; (ii) RCHO; (iii) +H<sup>+</sup>, -H<sub>2</sub>O.

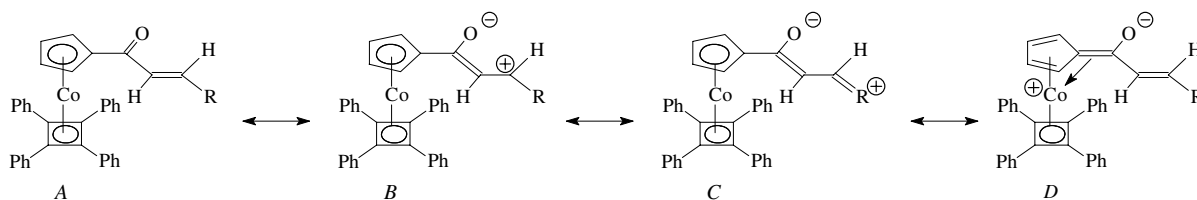
The spectra of the two pentadiene-1-one derivatives **3e** and **3g** show three strong absorption bands in this region which are attributed to the  $\nu(\text{CO})/\nu(\text{C}=\text{C})$  vibrations of the  $\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-$  group. In the case of **3e** with its  $\text{C}_6\text{H}_5$  end-group, these three bands have wavenumbers (relative intensities) of 1645 (10), 1595 (10), 1583 (15.5), but for **3g** where  $\text{Ar} = 4\text{-Me}_2\text{NC}_6\text{H}_4$  they are 1642 (10), 1602 (8.5), 1565 (23.6). These low frequencies and the high intensity of the  $1565\text{ cm}^{-1}$  band of **3g** are probably a consequence of the presence of the donor  $\text{Me}_2\text{N}$  group and a strong  $\text{Me}_2\text{N}-\pi\text{-C}(\text{O})$  donor-acceptor interaction with its consequent lessening of the bond-order alternation along the  $\pi$  chain. A similar effect is observed when the IR spectra of  $\text{C}_6\text{H}_5\text{CHO}$  ( $1684\text{ cm}^{-1}$ ) and  $[4\text{-Me}_2\text{NC}_6\text{H}_4\text{CHO}]$  ( $1661$  (10),  $1601$  (13.5)  $\text{cm}^{-1}$ ) are compared. The  $\nu(\text{CO})$  vibration of **3d** ( $1654\text{ cm}^{-1}$ ) has a much lower energy than that of  $[\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CHO}]$  ( $1676\text{ cm}^{-1}$ ) which suggests that there is an electronic interaction between the  $\text{C}=\text{O}$  and  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4-\}$  groups and that resonance forms such as **C** contribute to an overall description of the electronic structures of **3** (Fig. 8).

The IR spectra of the alcohols **4a** and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH}\}]$  which possess neither  $\text{C}=\text{O}$  nor  $\text{C}=\text{C}$  show only very weak bands between  $1500$  and  $1700\text{ cm}^{-1}$  as does the allylic alcohol  $[(\eta^4\text{-C}_4\text{Ph}_4)\text{Co}\{\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{OH})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7-1\}]$  (**4b**).

The NMR spectra of **3** are consistent with their structures. All except **3c** contain two multiplet  $^1\text{H}$  resonances at ca.  $\delta$  5.27–5.44 and 4.80–4.95 characteristic of the  $\text{Co}\{\eta^4\text{-C}_5\text{H}_4\text{C}(\text{O})-\}$  group. The NOESY correlation for **3d** confirms that the former are due to  $\text{C}_\alpha\text{H}$ . The most intense resonances in all spectra are assignable to the phenyl groups of the  $\eta^4\text{-C}_4\text{Ph}_4$  ligand which often obscure  $^1\text{H}$  resonances of the  $\text{CH}=\text{CH}$  and  $\text{R}$  groups. However, the former can be detected and sometimes identified by using 2-D techniques. The most useful resonances are those due to the  $\text{CH}=\text{CH}$  and  $\text{CH}=\text{CH}-\text{CH}=\text{CH}$  protons. The

$^3J_{\text{HH}}$  coupling constants  $=\text{CH}-\text{CH}=\text{CH}-$  in **3e** and **3g** at ca. 11 Hz are normal but high, and the coupling constants  $\text{CH}=\text{CH}$  across the double bonds (ca. 15 Hz) indicates their *trans* configurations [12]. This is consistent with the structures found in the solid state for **3d**, **3e**, **3g**, **3h**, **3i** and **3k**, and suggests that these are retained in solution. The attribution of the more deshielded of the ethylenic proton resonances, generally found at  $\delta$  7.2–8.5, to  $-\text{CH}=\text{CH}-\text{C}(\text{O})$  is consistent with the assignment of the  $^1\text{H}$  NMR spectrum of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{CH}-\text{CHO})]$  which is rendered unambiguous by the  $=\text{CH}-\text{CHO}$  coupling. It has been confirmed for **3d** by correlation (HMBC) of  $\text{C}(\text{O})$  with the  $\delta$  6.69 resonance but not with that at  $\delta$  7.39, and by correlation (NOESY) of the  $\delta$  6.69 resonance with the cyclopentadienyl resonance at  $\delta$  5.34 (but not that at  $\delta$  4.86) whilst the  $\delta$  7.39 resonance correlates with neither cyclopentadienyl resonance. This also is consistent with the structures found in the solid state with their *cis*- $\text{C}=\text{C}-\text{C}=\text{O}$  moiety. These observations also aid the assignment of the  $\text{CH}=\text{CH}-\text{CH}=\text{CH}$  resonances in the spectra of **3e** and **3g**, and suggest that resonance forms such as **B** and **C** (Fig. 8) also contribute to an overall description of the electronic structures of **3**.

The chemical shifts for the  $\text{RCH}=\text{CHC}(\text{O})$  and  $\text{RCH}=\text{CHC}(\text{O})$  both decrease along the series  $\text{R} = \text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4-) < \text{C}_6\text{H}_5 < 1\text{-C}_{10}\text{H}_7 < 9\text{-C}_{14}\text{H}_9 < 1\text{-C}_{16}\text{H}_9$  with a very marked increase in the deshielding of  $\text{RCH}$  in going from  $\text{R} = \text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4-)$ ,  $\text{C}_6\text{H}_5$  and  $\text{C}_4\text{H}_3\text{S}$  ( $\delta$  ca. 7.2) to the more highly annelated  $\text{R} = \text{C}_{10}\text{H}_7$ ,  $\text{C}_{14}\text{H}_9$  and  $\text{C}_{16}\text{H}_9$  ( $\delta$  8.19–8.46). When  $\text{R} = \text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4-\}$  and  $\text{C}_6\text{H}_4\text{NMe}_2\text{-4}$ , the  $\text{RCH}=\text{CHC}(\text{O})$  protons are less deshielded than those for other **3**. When the spectra of **3f** and **3g** are compared with those of the related  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{-NEt}_2\text{-4}\}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4-\text{C}(\text{O})-(\text{CH}=\text{CH})_2-\text{C}_6\text{H}_4\text{NMe}_2\text{-4}\}]$ , respectively, the chemical shifts of the indicated protons of the ferrocenyl complexes are always

Fig. 8. Resonance forms of **3**.

more deshielded than those of their  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\}$  counterparts [1].

In the  $^{13}\text{C}$  NMR spectra the assignment of the resonances at  $\delta$  140 and 123 to the  $\text{CH}=\text{CH}-\text{C}(\text{O})$  and  $\text{CH}=\text{CH}-\text{C}(\text{O})$  atoms is consistent with the above arguments and are further confirmed by HMBC and HSQC correlations. These resonances are particularly easy to identify unambiguously in the spectra of **3a**, **3b** and **3c** with their  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\}$  and  $\text{Fe}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\}$  end-groups, but this is not always the case when aromatic end-groups are present.

The NMR spectra of the alcohols **4a** and **4b** show four  $^1\text{H}$  and five  $^{13}\text{C}$  resonances as a consequence of the chiral nature of the  $\text{C}(\text{Me})(\text{OH})(\text{Bu}^n)$  or  $\text{C}(\text{H})(\text{OH})(\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7)$  substituents on the cyclopentadienyl ligands. The  $\text{CH}=\text{CH}$  coupling constant for **4b** confirms that the *trans* conformation about the double bond is retained on reduction of the carbonyl group of **3d**.

The UV/Vis spectrum of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)(\eta^5\text{-C}_5\text{H}_5)]$  shows a very intense absorption band lying below 250 nm, a strong band at 274 nm and a very weak one at 412 nm. That of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4-\text{C}(\text{O})\text{Me}\}]$  is similar but also has an added prominent shoulder at 318 nm. The spectrum of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})-\text{CH}=\text{CH}-\text{C}_6\text{H}_5\}]$  (**3d**), is comparable to these in that it has a very intense absorption band lying below 250 nm, an intense band at 285 (38000) nm ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , in parentheses) with a marked shoulder at 310 nm and a much weaker band at 405 nm (2200). When the conjugated linker is increased by  $-\text{CH}=\text{CH}-$ , **3e**, an extra band appears at 344 nm (38000). When  $\text{C}_6\text{H}_5$  is replaced by  $4\text{-Me}_2\text{NC}_6\text{H}_4$  these bands red-shift to 418 nm (34000) for **3f** and to 431 nm (39900 br) for **3g**, and become broader as well as more intense. This behaviour is that expected for a donor- $\pi$ -acceptor system in which conjugated chain length is increased and the donor is replaced by a stronger one.

When the terminal phenyl group in **3d** is replaced by 1-naphthyl in **3i**, the 285 nm band is replaced by two bands at 257 (47400) and 278 nm (44400) and the 310 nm shoulder by a well-defined band at 347 nm (20800) which is absent from the spectrum of  $(\eta^4\text{-C}_4\text{Ph}_4)\text{Co}\{\eta^5\text{-C}_5\text{H}_4-\text{CH}(\text{OH})\text{CH}=\text{CH}-\text{C}_{10}\text{H}_7-1\}$  (**4b**). This suggests that the 354 nm band is due to  $\pi-\pi^*$  electronic transitions involving the molecule as a whole rather than just the aryl end-groups. On this basis it seems reasonable to suggest that the 310 nm shoulder of **3d** also arises from related  $\pi-\pi^*$  transitions as does the 410 (16400) nm band in the anthracenyl derivative **3k**, the pair of absorption bands at 389 (25800) and 419 (26100) nm in the spectrum of the pyrenyl complex **3l**, and the broad absorption band in the spectrum of the perylenyl derivative **3m** at 468 nm with its ill-defined shoulders at 424 and 452 nm. However, it is clear that as the annellation of the aryl end-group increases, the UV/Vis spectra of **3** increasingly resemble those of the parent polycyclic aromatic hydrocarbons [13], though without well-defined vibrational fine structure [14]. The absorption

bands of **3** generally have lower energies than those of the parent arene, but the difference becomes less marked as the complexity of the aryl group increases.

Absorption bands in the UV/Vis spectra of **3d** (283, 385 nm), **3e** (284, 344 nm) and **3i** (257, 278, 347 nm) have lower energies than those found in the spectra of their organic counterparts such as  $[\text{C}_6\text{H}_5-\text{CH}=\text{CHC}(\text{O})\text{Me}]$  (222, 285 nm),  $[\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}=\text{CHC}(\text{O})\text{Me}]$  (233, 319 nm) and  $[1\text{-C}_{10}\text{H}_7-\text{CH}=\text{CHC}(\text{O})\text{Me}]$  (233, 251, 334 nm) [15]. This is consistent with the proposed electronic interaction between the  $\text{C}=\text{O}$  and  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\}$  groups and the contribution of resonance forms such as **C** to an overall description of the electronic structures of **3** (Fig. 8).

These observations suggest that **3** are typical donor- $\pi$ -acceptor chromophores with two donors. Increasing the annellation of the aryl end-group means that the energy of its LUMO falls and its HOMO increases so that the HOMO and LUMO of the whole molecule becomes increasingly dominated by the aryl end-group.

### 3.2. Structures of $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$ , [*R* = (d) $\text{C}_6\text{H}_5$ , (e) $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ , (g) $\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2-4$ , (h) $3\text{-C}_4\text{H}_3\text{S}$ , (i) $1\text{-C}_{10}\text{H}_7$ , and (k) $9\text{-C}_{14}\text{H}_9$ ]

X-ray diffraction has been used to determine the crystal and molecular structures of **3d**, **3e**, **3g**, **3h**, **3i** and **3k**. The structures and atom labelling are shown in Figs. 1–6. All six molecules contain a Co atom sandwiched between  $\eta^4\text{-C}_4\text{Ph}_4$  and  $\eta^5\text{-C}_5\text{H}_4$  ligands with the cyclopentadienyl ligand as part of a  $\text{C}_5\text{H}_4-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{R}$  or  $\text{C}_5\text{H}_4-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{R}$  system which has an all-*trans* conformation. The two cyclic ligands are almost parallel with dihedral angles of 0–3.9° between them. They may be oriented such that one carbon bond of the cyclobutadiene is parallel to one of the three different types of C–C bonds of the substituted cyclopentadienyl ligand, (a)–(c) in Fig. 9, and or so that one C atom of the cyclobutadiene eclipses a C atom of the cyclopentadienyl ligand, (d)–(f) in Fig. 9. Compound **3k** adopts orientation (a), **3i** adopts orientation (b), **3d**, **3g** and **3h** adopt orientation (c), and **3e** adopts orientation (f).

The Co–C(cyclopentadienyl) distances lie in the range 2.0528(18)–2.102(5) Å. They are always significantly longer than Co–C(cyclobutadiene) 1.9634(15)–2.0026(18) Å and show greater variation, but the differences between the Co–centroid distances are much smaller and in the opposite sense with 1.675–1.687 Å to the cyclopentadienyl ligand and 1.688–1.702 Å to the cyclobutadiene. C–C bond lengths within the cyclopentadienyl ring, 1.400(8)–1.441(6) Å, are shorter than those within the cyclobutadiene, 1.456(3)–1.480(4) Å, and the C–C(cyclopentadienyl) bonds to  $\text{C}^*-\text{C}(\text{O})$  are longer, 1.422(6)–1.440(7) Å, than the other three, 1.400(8)–1.425(3) Å, but shorter than  $\text{C}^*-\text{C}(\text{O})$ , 1.469(2)–1.486(3) Å.

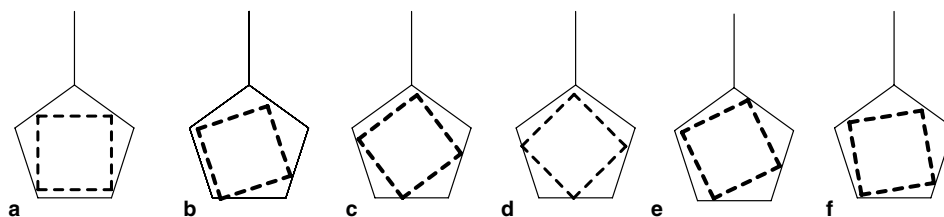


Fig. 9. Relative orientations of cyclopentadienyl and cyclobutadiene ligands in **3**.

The phenyl rings of the  $C_4Ph_4$  ligands of  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4-R\}]$  where  $R = CHO, C(O)Me, CH(OH) (Bu')$  [2] are all tilted with respect to the plane of the cyclobutadiene ligand and in the same sense so that these  $C_4Ph_4$  constitute a four-bladed propeller. A similar arrangement is observed in **3d** and **3h** with dihedral angles between cyclobutadiene and phenyl rings of 28.9–36.6° and 29.0–36.2°, respectively, and in **3k** where the dihedral angles are all different at 42.1° to C(5), 25.5° to C(11), 30.4° to C(17) and 54.5° to C(23), as they are in **3g** at 19.0° to C(5), 57.5° to C(11), 47.1° to C(17) and 34.1° to C(23). In **3e**, on the other hand, the phenyl group which is almost eclipsed by the cyclopentadienyl substituents, C(5)–C(10) and its *trans* partner are almost coplanar with the  $C_4$  ring (dihedral angles of 10.2° and 6.3°, respectively), whilst the other two show dihedral angles of 51.3° and 67.6° with respect to it and are tilted in opposite senses, i.e., they are close to coplanar. These differing conformations of the phenyl groups in the  $C_4Ph_4$  ligand are probably the consequence of the presence of the  $C(=O)-(CH=CH)_n-R$  substituent on the cyclopentadienyl ligand which, together with crystal packing forces, perturb the Ph–Ph steric interactions.

The  $C(Cp)-C(=O)-CH=C^*H-R$  and  $C(Cp)-C(=O)-CH=CH-CH=C^*H-R$  systems have *trans* configurations about their  $C=C$  bonds. The  $C-C-C$  bond angles at the carbonyl carbon C(34) are close to 118° whilst those at  $C^*$  are close to 126°. The remaining angles in the  $-C(O)(CH=CH)_n-$  lie between these two extremes. The  $C-C$  and  $C=C$  bond lengths lie in the ranges 1.459(2)–1.486(7) Å and 1.330(2)–1.339(2) Å, respectively. These are comparable with the bond lengths found for  $[(\eta^5-C_5H_5)Fe\{\eta^5-C_5H_4-C(O)-(CH=CH)_n-C_6H_4NEt_2-4\}]$  ( $n = 1, 2$ ) and related systems [1,16]. The presence of the strong donor group  $NMe_2$  in **3g** does not greatly affect the bond alternation in the  $C_4H_4$  fragment as compared with **3g**. However, it does affect the phenyl ring which in **3e** has  $C-C$  distances which vary randomly between 1.383(3) Å and 1.402(3) Å, whilst in **3g** there is a quinonoid distortion {1.405(3)–1.424(3) Å versus 1.376(3), 1.377(3) Å} and a planar  $NMe_2$  group with a short  $C-NMe_2$  bond. This is convincing evidence for charge separation along the conjugate chain (mesomer *C* in Fig. 8) with a positively charged N atom.

The  $\eta^5-C_5H_4-C(=O)-(CH=CH)_nR$  moieties are not planar. In **3i**,  $C_5H_4-C(=O)-CH=CH$  and naphthyl fragments are planar with an angle of 31° between them,

whereas in **3e** it is  $C(35)-C=C-C=C-C_6H_5$  which constitute a plane with no atom more 0.06 Å from it with angles between this plane, and  $C(35)-C(=O)-C(29)$  and  $C_5H_4$  of 17.4° and 16.1°, respectively. In the closely related **3g** with its strong donor end-group the angle between the  $C_6H_4NMe_2$ ,  $C(29)-C(O)-CH=CH-CH=CH-C(39)$  and  $C_5H_4$  planes are, respectively, 17.1° and 10°. In **3d** and **3h** the angles between the  $C_5H_4$ , C(5)–C(=O)–C(11), C(10)–C=C–C(13) and phenyl/thiophenyl fragments are 8.4°, 10°, 7.6° and 7.5°, 8.2°, 13.1°, respectively. However, it is in **3k** that distortions from complete planarity are most marked.  $C(29)(=O)-C=C$  is planar but the anthracenyl C(37) lies below that plane and the dihedral angles between it and the planar cyclopentadienyl and anthracenyl groups are 14.8° and 51.1°, respectively. Although the non-planarity in the case of **3d**, **3e**, **3h** and **3i** may be a consequence of crystal packing forces, it seems reasonable to assume that for **3k** the distortions are due to intramolecular steric interactions between the anthracenyl group and the C(36) hydrogen atom on one hand, and the phenyl groups of the  $C_4Ph_4$  ligand on the other. In a related complex  $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-CH=CH-9-anthracenyl)$  similar anthracene–alkene steric interactions are relieved by rotation about the  $C-C$  bond joining them so that there is an angle of 62.58(14)° between alkene and anthracene planes [17]. The presence of the phenyl groups of the tetraphenylbutadiene ligand prevents this in **3k**.

### 3.3. $[Co\{\eta^4-Ph(H)C(Ph)C(Ph)C(H)Ph\}\{\eta^5-C_5H_4C(O)CH_3\}]$ (**1c**)

Compound **1c** is formed during the preparation and purification of  $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)CH_3\}]$  (**1a**), and isolated in yields of ca. 1%. A related complex,  $[Co\{\eta^4-Ph(H)CC(Ph)C(Ph)C(H)Ph\}(\eta^5-C_5H_5)]$ , has been reported and characterised previously. It was obtained on the electrochemical reduction of  $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_5)]$  [18]. Consequently, it seems reasonable to assume that, in our case, the tetraphenylbutadiene ligand was formed by the reductive ring-opening of the  $\eta^4$ -tetraphenylcyclobutadiene of **1a**. TLC monitoring of the reaction that formed **1a** suggested that **1c** was not present in the reaction mixture prior to chromatography but we cannot be completely certain of this because it is formed in such low yields. However, acids have been shown to open the tetramethylcyclobutadiene ligand of  $[Co(\eta^4-C_4Me_4)(\eta^5-C_5H_5)]$  to give the tetramethylbutenyl cation  $[Co\{\eta^3-C_4Me_4H\}(\eta^5-C_5H_5)]^+$  which



can be reduced by hydride sources to the tetramethylbuta-1,3-diene complex  $[\text{Co}\{\eta^4\text{-Me(H)CC(Me)C(Me)C(H)-Me}\}(\eta^5\text{-C}_5\text{H}_5)]$  [19]. Consequently, it is possible that **1c** was formed from **1a** in a similar way during work-up of the reaction mixture, perhaps with the acid coming from the dichloromethane used in chromatography.

The IR and NMR spectra of **1c** are consistent with its structure but do not define it. The  $\nu(\text{CO})$  vibration of the acetyl group gives rise to an IR absorption band at  $1662\text{ cm}^{-1}$  compared with  $1672\text{ cm}^{-1}$  for **1a** and  $1684\text{ cm}^{-1}$  for benzaldehyde. Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show the expected resonances due to the acetylcyclopentadienyl ligand, two types of phenyl groups and the  $\text{CH}=\text{C}-\text{C}=\text{CH}$  part of the  $\eta^4$ -butadiene ligand (cf. Ref. [20]).

The molecular structure of **1c** is similar to that of  $[\text{Co}\{\eta^4\text{-Ph(H)CC(Ph)C(Ph)C(H)Ph}\}(\eta^5\text{-C}_5\text{H}_5)]$  [20,21]. It, together with its atom labelling, is shown in Fig. 7. The Co atom is sandwiched between a  $\eta^5$ -acetylcyclopentadienyl and a  $\eta^4$ -1,3-tetraphenylbutadiene ligand. Although the C(1)–C(4) and C(29)–C(33) moieties of the cyclopentadienyl and butadiene ligands are planar, they are not parallel, and there is a dihedral angle of  $14.7^\circ$  between them. The terminal Ph–C–H moieties of the butadiene ligand are not coplanar with the C(1)–C(4) plane but make dihedral angles of  $33.7^\circ$  and  $35.4^\circ$  with it so that both Ph groups adopt the *exo* configuration and are tilted towards the cyclopentadienyl ligand. In contrast, the *ipso* C atoms of the central Ph groups lie close to the C(1)–C(4) plane though the rings are tilted with respect to it by  $64.0^\circ$  for C(11) and  $77.3^\circ$  for C(17). The Co–C(butadiene) distances are  $2.0594(15)/2.0485(15)\text{ \AA}$  to the outer C atoms and  $1.9911(15)/1.9874(15)\text{ \AA}$  to the inner (cf.  $1.9742(15)$ – $1.9885(16)\text{ \AA}$  to the cyclobutadiene ligand in **1a**). The C–C distances within the *cis*-butadiene ligand are similar at  $1.432(2)/1.431(2)\text{ \AA}$  for the outer bonds and  $1.4494(19)\text{ \AA}$  for the inner (cf.  $1.458(2)$ – $1.474(2)\text{ \AA}$  for the cyclobutadiene ligand in **1a**). These compare with  $1.357(4)\text{ \AA}$  (outer) and  $1.501(4)\text{ \AA}$  found in the silacyclopentadiene  $[\text{Ph}_4\text{C}_4\text{SiPh}_2]$  [22], a surrogate for *cis*-1,2,3,4-tetraphenylbutadiene, and  $1.441(3)$ ,  $1.445(3)\text{ \AA}$  (outer) and  $1.442(3)\text{ \AA}$  in the tetraphenylsilacyclopentadiene-tricarbonyliron derivative  $[\text{Fe}(\text{CO})_3\{\eta^4\text{-Ph}_4\text{C}_4\text{Si}(\text{Cl})\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}]$  [23], a surrogate for its  $\text{Fe}(\text{CO})_3$  complex.

#### 4. Conclusions

In aqueous ethanol, NaOH promotes the Claisen–Schmidt condensation reaction between  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  or acetophenone and  $[\text{C}_6\text{H}_5\text{CHO}]$  or  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CHO})$  [1c,1g,1h,24] to give the corresponding chalcones  $\text{R}'\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}$ , but in our hands it fails to bring about the corresponding reaction of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  with  $[\text{C}_6\text{H}_5\text{CHO}]$  or  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$ . This implies that the methyl protons in  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$

are less acidic than those in  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  or  $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_3]$  and can only be removed by a stronger base such as NaH. This promotes the condensation of  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3\}]$  with aromatic aldehydes,  $[\text{RCHO}]$  (**2a–m**), to give  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$  and  $[\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{R}\}]$  (**3**), all of which have a *trans* configuration about their C=C double bonds. These compounds are very similar to their ferrocenyl counterparts,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{R}\}]$  and  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{R}\}]$ , respectively. Although their spectroscopic properties suggest that **3** are donor–acceptor–donor systems in which the  $\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)\{\eta^5\text{-C}_5\text{H}_4\text{-}\}$  and aryl groups act as donors to the carbonyl groups, the electronic interactions appear to be relatively limited and do not result in planar molecules or single bond–double bond equalisation.

#### 5. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 285138 (**1c**), 285136 (**3d**), 285139 (**3e**), 285142 (**3g**), 285137 (**3h**), 285141 (**3i**), and 285140 (**3k**).

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