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Stilbene analogues incorporating the $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4-)$ end group

Paul O'Donohue^a, C. John McAdam^{b,*}, Donagh Courtney^a, Yannick Ortin^a, Helge Müller-Bunz^a, Anthony R. Manning^a, Michael J. McGlinchey^a, Jim Simpson^b

^a School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland
^b Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054, New Zealand

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ABSTRACT

A number of organometallic stilbenes of the general type $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR]$ are reported where R is C_6H_4X-4 (X = H, OMe, Br, NO₂), 1-naphthyl, 9-anthryl, 1-pyrenyl, ($\eta^5-C_5H_4$)Co($\eta^4-C_4Ph_4$), and $(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4Y)$ {Y = CHO, CH=C(CN)₂ and CH=CHC₅H₄- η^5)Co $(\eta^4-C_4Ph_4)$ }. They were prepared by Wittig or Horner–Wadsworth–Emmons reactions which yield both E and Z or only E products respectively. The isomers were separated and all compounds characterised by standard spectroscopic techniques as well as by X-ray diffraction methods in many cases. The electrochemistry of the stilbene analogues in dichloromethane solution is also reported. In most, the $(\eta^5-C_5H_4)Co(\eta^4-C_4Ph_4)$ functional group undergoes a reversible one-electron oxidation. For those molecules that also include $(n^5-C_5H_4)Fe$ $(\eta^5-C_5H_4Y)$, this is preceded by the reversible oxidation of the ferrocenyl group. Spectroscopic and structural data suggests that for most compounds there is little electronic interaction between $Co(\eta^4$ - C_4Ph_4 (η^5 - C_5H_4) and the R end groups which are effectively independent of one another. The only exceptions to this are Z and E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₆H₄NO₂-4], and [Co(η^4 -C₄Ph₄)(η^5 - $C_5H_4CH = CHC_5H_4 - \eta^5)Fe\{\eta^5 - C_5H_4CH = C(CN)_2\}$ where the electronic spectra are respectively consistent with a significant $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4)/NO_2$ donor/acceptor interaction and a less significant $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4)/NO_2$ $C_4Ph_4)(\eta^5-C_5H_4)/C(CN)_2$ one. However, OTTLE studies show that in the electronic spectra of $[Co(\eta^4 C_4Ph_4)(\eta^5-C_5H_4CH=CHR]^+$ there are low energy absorption bands (950–1800 nm) which are attributed to $R \rightarrow Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4)^+$ or, when R is a ferrocenyl-base group, $Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4) \rightarrow (\eta^5 - C_5H_4)^+$ C_5H_4)Fe(η^5 - C_5H_4 Y)⁺ charge transfer transitions. The ferrocenyl compounds undergo cis/trans isomerisation on the OTTLE experiment timescale.

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1. Introduction

Stilbenes and stilbenoids are an important class of compounds based on 1,2-diarylethenes [1–4]. Their photochemical and photophysical properties have been studied in detail [1], and they have many uses and roles based on these properties. For example, they act as the π -spacer in D(onor)- π -A(cceptor) systems such as the NLO-active DANS, 4-Me₂NC₆H₄CH=CHC₆H₄NO₂-4' [5]; they form the basis of many dyes and optical brighteners (e.g. DAS or DAST, 4,4'-diaminostilbene-2,2'-disulphonic acid) [2,3]; many are present naturally in plants (e.g. resveratrol or *trans*-3,5,4'-trihydroxystilbene) [4]; and others are synthetic oestrogens (e.g. diethylstilbestrol) [6].

Of particular interest to us are those stilbenes where one or both aryl groups have been replaced by pseudo-aromatic organometallic groups. We have reported detailed spectroscopic, structural, electrochemical and theoretical studies on $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CH=CHR)]$ derivatives where R is phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthryl, 9-anthryl, 1-pyrenyl and 3-perylenyl) [7,8], and on the mixed metal stilbenoid $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Co(\eta^4-C_4Ph_4)]$ [9]. Herein we describe the preparation, spectra, structures and electrochemisty of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR)]$ complexes where R is C_6H_4X-4 (X = H, OMe, Br, NO₂), 1-naphthyl, 9-anthryl, 1-pyrenyl, $(\eta^5-C_5H_4)Co(\eta^4-C_4Ph_4)$, and some $(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4X)$ where X = CHO, CH=C(CN)₂ and (CH=CHC_5H_4-\eta^5)-Co(\eta^4-C_4Ph_4). Previously we have described *E*-[Co($\eta^4-C_4Ph_4$)($\eta^5-C_5H_4CMe=CMeC_5H_4-\eta^5$)Co($\eta^4-C_4Ph_4$)] prepared from $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4C(O)Me\}]$ by McMurry coupling [10].

2. Experimental

Unless otherwise stated, all reactions were carried out at room temperature under nitrogen in dried and deoxygenated solvents.

^{*} Corresponding author. Tel.: +64 3 479 4897; fax: +64 3 479 7906. *E-mail address:* mcadamj@alkali.otago.ac.nz (CJ. McAdam).

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Previously reported procedures or closely related ones were used to prepare [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CHO)](1)[11 and refs therein], [Co (η^4 -C₄Ph₄){ η^5 -C₅H₄CH₂P(O)(OEt)₂}] (2) [12], [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH₂PPh₃)]Cl, [3]Cl, [12], [FcCH₂PPh₃]I, {Fc = ferrocenyl = Fe (η^5 -C₅H₅)(η^5 -C₅H₄-} [13], 9-anthracenecarboxaldehyde [14], 1-pyrenecarboxaldehyde [15], and [Fe(η^5 -C₅H₄CHO)₂] [16]. Other reagents were purchased from commercial sources unless otherwise stated.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR spectrometer, and NMR spectra on Varian Inova 300, 400 or 500 MHz spectrometers. ¹H (300 and 400 MHz), and ¹³C (75 and 100 MHz) chemical shifts are reported downfield from tetrame-thylsilane as the internal standard. All coupling constants are given in Hertz. UV/Visible spectra were recorded on a UNICAM UV2 spectrometer. Elemental analyses were performed in the Micro-analytical Laboratory, University College Dublin.

Cyclic voltammetric experiments were carried out at 20 °C in CH₂Cl₂ solutions degassed with nitrogen. A three-electrode cell was used with Cypress Systems 1 mm diameter Pt or 1.4 mm glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. Solutions were ~ 10^{-3} M in electroactive material and contained 0.1 M [Bu₄N][PF₆] as the supporting electrolyte. Voltammograms were recorded using a Powerlab/4sp computer-controlled potentiostat. All potentials are referenced to the reversible formal potential (taken as $E^{\circ} = 0.00$ V) for the [Fe(η^{5} -C₅Me₅)₂]^{+/0} process [17] where E° was calculated from the average of the oxidation and reduction peak potentials under conditions of cyclic voltammetry. Under the same conditions, E° calculated for [Fe(η^{5} -C₅H₅)₂]^{+/0} was 0.55 V.

2.1. Preparation of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_6H_4X-4)], (X = H, 4a; OMe, 4b; Br, 4c; NO_2, 4d), and <math>[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_{10}H_7-1)]$ (1- $C_{10}H_7$ = 1-naphthyl), 4e by the Wittig reaction

n-BuLi in hexane (0.87 ml, 1.38 mmol) was added to a solution of [PhCH₂PPh₃]Br (0.897 g, 2.1 mmol) in dry THF (50 ml) at $-78 \,^{\circ}$ C, and the mixture stirred at this temperature for 30 min. It was allowed to warm to room temperature and solid [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CHO)], **1**, (0.350 g, 0.69 mmol) added. The mixture was refluxed overnight, quenched with water and extracted with CH₂Cl₂. The organic layer was separated, dried over magnesium sulphate and concentrated. The isomers were separated by column chromatography on silica (cyclohexane-toluene; 9:1) and crystallised from a dichloromethane-pentane solution to give *Z*-**4a** (Yield 0.105 g, 26%) and *E*-**4a** (Yield 0.165 g, 41%).

The same procedure was used to prepare, separate and purify the following:

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_6H_4OMe-4)]$, **4b**. From n-BuLi in hexane (0.52 ml, 0.83 mmol), [4-MeOC_6H_4CH_2PPh_3]Br (0.519 g, 1.24 mmol) and $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$ (0.210 g, 0.41 mmol). The isomers were separated by column chromatography on silica (cyclohexane-toluene; 4/1) and crystallised from dichloromethane-pentane to give *Z*-**4b** (34%) and *E*-**4b** (33%).

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_6H_4Br-4)]$, **4c**. From n-BuLi in hexane (0.43 ml, 0.71 mmol), $[4-BrC_6H_4CH_2PPh_3]Br$ (0.403 g, 0.79 mmol) and $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$ (0.200 g, 0.39 mmol). The isomers were separated by column chromatography on silica (pentane-dichloromethane; 5/1) and crystallised from dichloromethane-pentane to give *Z*-**4c** (0.093 g, 36%) and *E*-**4c** (0.098 g, 38%).

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_6H_4NO_2-4)]$, **4d**. From n-BuLi in hexane (0.63 ml, 1.0 mmol), $[4-NO_2C_6H_4CH_2PPh_3]Br$ (0.576 g, 1.0 mmol) and $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$ (0.200 g, 0.39 mmol) (0.25 g, 0.49 mmol). The isomers were separated by column chromatography on silica (pentane-toluene; 1/1) and crystallised from

dichloromethane-pentane to give *Z*-**4d** (0.092 g, 30%) and *E*-**4d** (0.122 g, 40%).

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_{10}H_7-1)](C_{10}H_7 = naphthyl), 4e.$ From n-BuLi in hexane (0.3 ml, 1.2 mmol), $[1-C_{10}H_7CH_2PPh_3]Cl$ (0.780 g, 1.6 mmol) and $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO)]$ (0.300 g, 0.59 mmol). The isomers were separated by column chromatography on silica (cyclohexane-toluene; 9/1) and crystallised from dichloromethane-pentane to give *Z*-4e (0.033 g, 9%) and *E*-4e (0.109 g, 29%).

2.2. Preparation of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR)]$, $[R = 9-C_{14}H_9 = 9$ -anthryl, **4f**; $1-C_{16}H_9 = 1$ -pyrenyl, **4g**; and $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4-1)$, **5**], and $[\{Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)\}_2Fe]$, **9**, by the Horner–Wadsworth–Emmons reaction

To a cooled solution $(-78 \degree C)$ of $[Co(\eta^4-C_4Ph_4){\eta^5-C_5H_4CH_2P(O) (OEt)_2}]$, **2**, (0.320 g, 0.50 mmol) in dry THF (35 ml) was added t-BuLi in pentane (0.31 ml, 0.40 mmol) and, after 1 h, 9-C₁₄H₉CHO (0.100 g, 0.48 mmol). The mixture was stirred for a further hour, allowed to return to room temperature and stirred overnight. The reaction was quenched with water and extracted with dichloromethane. The organic layer was separated, dried over MgSO₄, filtered and column chromatographed on silica (dichloromethane-pentane; 1/2). The first band gave red-brown crystals which were precipitated from a dichloromethane-pentane solution and identified as *E*-**4f** (0.090 g, 33%). The second band gave an orange powder from a dichloromethane-pentane solution which was identified as **5** (0.018 g, 4%).

The same procedure was used to prepare:-

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_{16}H_9-1)]$ ($C_{16}H_9-1 = 1$ -pyrenyl), **4g**. From t-BuLi in pentane (0.24 ml, 0.4 mmol), $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4CH_2P(O)(OEt)_2\}]$ (0.320 g, 0.5 mmol), and $1-C_{16}H_9CHO$ (0.092 g, 0.4 mmol). The products were separated by column chromatography on silica (pentane-toluene; 3/2), and crystallised from dichloromethane-pentane solutions to give red-brown crystals of *E*-**4g** (0.055 g, 19%) and orange **5** (0.017 g, 4%).

 $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Co(\eta^4-C_4Ph_4)]$, **5**. From t-BuLi in pentane (0.22 ml, 0.38 mmol), $[Co(\eta^4-C_4Ph_4)\{\eta^5-C_5H_4CH_2P(O)(OEt)_2\}]$ (0.260 g, 0.41 mmol) and $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO](0.254 g, 0.5 mmol)$. The product was purified by column chromatography on silica (dichloromethane-pentane; 3/5) and orange crystals of *E*-**5** grown from a chloroform-pentane solution (0.065 g, 16%).

[{Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)}₂ Fe], **9**. From t-BuLi in pentane (0.11 ml, 0.18 mmol), [Co(η^4 -C₄Ph₄){ η^5 -C₅H₄CH₂P(O) (OEt)₂}] (0.130 g, 0.21 mmol) and [Fe(η^5 -C₅H₄CHO)₂] (0.025 g, 0.1mmol). Two products were separated by chromatography on silica (dichloromethane-pentane; 3/5) and crystallised from dichloromethane-pentane solutions to give orange-red *E*,*E*-**9** (0.025 g, 21%) and orange **5** (0.007 g, 4%).

2.3. Preparation of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Fe(\eta^5-C_5H_4CHO)]$, **7**, by the Wittig reaction

To a solution of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH_2PPh_3)]Cl$, **[3**]Cl, (0.40 g 0.51 mmol) in dry THF (15 ml) at $-78 \degree C$ was added n-BuLi in hexane (0.31 ml, 0.45mmol) and, after 2 h, solid $[Fe(\eta^5-C_5H_4CHO)_2]$ (0.120 g 0.51 mmol). After a further 1 h, the mixture was warmed to room temperature and stirred overnight. It was quenched with water and extracted with dichloromethane. The organic layer was separated, dried over magnesium sulphate, filtered, concentrated and chromatographed on silica (dichloromethane). One red band was obtained which was shown to be a mixture of *Z* and *E* isomers of **7** by NMR spectroscopy. Red-orange crystals of the pure *Z* isomer precipitated from a dichloromethane-pentane solution (0.110 g, 34%).

| Table 1a | | | | | | |
|--------------|--------------------|----------------|----------------|----------------|-----|----------------|
| Crystal data | for E- 4a , | E- 4b , | E- 4c , | E- 4d , | and | E- 4e . |

| Compound | E- 4 a | E- 4 b | E- 4c | E- 4d | E- 4e |
|---|------------------------------------|-------------------------------------|--------------------------------------|--|------------------------------------|
| Empirical formula | C ₄₁ H ₃₁ Co | C ₄₂ H ₃₃ OCo | C ₄₁ H ₃₀ CoBr | C ₄₁ H ₃₀ NO ₂ Co | C ₄₅ H ₃₃ Co |
| Formula weight | 582.59 | 612.61 | 661.49 | 627.59 | 632.64 |
| Temperature | 293(2) K | 293(2) K | 100(2) K | 100(2) K | 293(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic | Triclinic |
| Space group | P21/c | P-1 | P21/c | P-1 | P-1 |
| Unit cell dimensions (Å), (°) | a = 11.3993(15) | a = 10.3708(15) | a = 8.7371(7) | a = 16.4543(9) | a = 11.5130(14) |
| | b = 15.383(2) | b = 11.4773(17) | b = 57.863(5) | b = 17.3347(10) | b = 12.1254(15) |
| | c = 16.962(2) | c = 14.889(2) | c = 17.7746(15) | c = 19.1133(11) | c = 12.2446(15) |
| | $\alpha = 90$ | $\alpha = 79.517(2)$ | $\alpha = 90$ | $\alpha = 68.677(2)$ | $\alpha = 84.916(2)$ |
| | $\beta = 98.457(2)$ | $\beta = 70.378(2)$ | $\beta = 90.581(2)$ | $\beta = 64.746(2)$ | $\beta = 82.227(2)$ |
| | $\gamma = 90$ | $\gamma = 69.945(2)$ | $\gamma = 90$ | $\gamma = 71.731(2)$ | $\gamma = 71.843(2)$ |
| Volume (Å ³) | 2942.0(7) | 1563.6(4) | 8985.6(13) | 4511.3(4) | 1607.3(3) |
| Z | 4 | 2 | 12 | 6 | 2 |
| Density calculated (Mg/m ³) | 1.315 | 1.301 | 1.467 | 1.386 | 1.307 |
| Absorption coefficient (mm ⁻¹) | 0.612 mm^{-1} | 0.582 mm^{-1} | 1.936 mm ⁻¹ | 0.610 mm^{-1} | 0.566 mm^{-1} |
| F(000) | 1216 | 640 | 4056 | 1956 | 660 |
| Crystal size (mm) | $1.00\times0.10\times0.01$ | $0.60\times0.40\times0.20$ | $0.50 \times 0.20 \times 0.03$ | $0.60 \times 0.60 \times 0.20$ | $0.40 \times 0.30 \times 0.30$ |
| θ range for data collection | 1.80-24.00°. | 1.89–28.49°. | 1.20-20.84°. | 1.28–39.35°. | 1.68–28.32°. |
| Index ranges | -13<=h<=13, | -13<=h<=13, | -8<=h<=8, | -29<=h<=29, | -15<=h<=14, |
| - | -17<=k<=17, | -14<=k<=15, | -57<=k<=57, | -30<=k<=30, | -16<=k<=16, |
| | -19 <= l <= 19 | -19 <= l <= 19 | -16 <= l <= 17 | -33<=l<=33 | -16 <= l <= 16 |
| Reflections collected | 18777 | 26597 | 32919 | 183650 | 13851 |
| Independent reflections | 4607 [R(int) = 0.0509] | 7317 [R(int) = 0.0266] | 9409 [R(int) = 0.0449] | 51066 [R(int) = 0.0224] | 7233 [R(int) = 0.0166] |
| Completeness to $\theta = 24.0^{\circ}$ | 100.0% | 92.5% | 99.7% | 95.1% | 90.4% |
| Absorption correction | Semi-empirical from | Numerical | Semi-empirical from | Semi-empirical from | Numerical |
| | equivalents | | equivalents | equivalents | |
| Max. and min. transmission | 0.9939 and 0.7215 | 0.8926 and 0.7217 | 0.9442 and 0.7129 | 0.8878 and 0.7484 | 0.8486 and 0.8053 |
| Refinement method | Full-matrix least-squares | Full-matrix least-squares | Full—matrix least-squares | Full-matrix least-squares | Full-matrix least-squares |
| | on F ² | on F ² | on F ² | on F ² | on F ² |
| Data/restraints/parameters | 4607/0/379 | 7317/0/529 | 9409/534/1162 | 51066/0/1576 | 7233/0/547 |
| Goodness–of–fit on F ² | 1.006 | 1.052 | 1.220 | 1.035 | 1.069 |
| Final R indices [I > 2sigma | R1 = 0.0452, $wR2 = 0.0958$ | R1 = 0.0409, wR2 = 0.1073 | R1 = 0.0644, $wR2 = 0.1287$ | R1 = 0.0451, $wR2 = 0.1218$ | R1 = 0.0472, w $R2 = 0.1112$ |
| R indices (all data) | R1 = 0.0744, $wR2 = 0.1055$ | R1 = 0.0485, wR2 = 0.1133 | R1 = 0.0769, $wR2 = 0.1330$ | R1 = 0.0600, $wR2 = 0.1317$ | R1 = 0.0568, wR2 = 0.1176 |
| Largest diff. peak and hole $(e.Å^{-3})$ | 0.359 and -0.190 | 0.661 and -0.201 | 1.249 and -0.592 | 1.851 and -0.500 | 0.456 and -0.159 |

2.4. Preparation of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Fe\{\eta^5-C_5H_4CH=C(CN)_2\}]$, **8**

A drop of triethylamine was added to a solution of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₄CHO)], Z-**7**, (0.030 g, 0.042 mmol) and malononitrile (0.003 g, 0.045 mmol) in dichloromethane (10 ml), and the mixture was stirred overnight. It was filtered through a small pad of Celite and the filtrate chromatographed on silica (pentane-dichloromethane; 2/1). The product was eluted as a red band and dark red crystals of **8** were obtained from a pentane-dichloromethane solution (0.026 g, 81%).

2.5. Characterisation

2.5.1. Z-[$Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_5)$], Z-**4a**

m.p. 157–159 °C (Found: C 84.13, H 5.32, Co 10.50; C₄₁H₃₁Co requires C 84.51, H 5.37, Co 10.11%). IR ν /cm⁻¹: ν (C=C) 1597, 1498 (CH₂Cl₂); ν (C=C) 1597, 1498 (KBr). ¹H NMR (CDCl₃): δ 7.40–7.10 (m, 25H, *Ph*, C₆H₅); 6.24 and 5.64 [2 × (d, ³J_{H,H} 12 Hz, 1H, CH=CH)]; 4.53 (s, 4H, C₅H₄). ¹³C NMR (CDCl₃): δ 138.1 (C_i , C₆H₅); 136.2, 128.9, 128.0 and 126.2 (C₄*Ph*₄); 129.3, 128.8 and 128.1 (CH, C₆H₅); 126.8 and 124.7 (CH=CH); 93.3 (C_{ipso} , C₅H₄), 84.4 and 83.1 (CH, C₅H₄); 75.3 (C₄Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 241 (33), 267 (30), 310 (27), 398 (4.1); (CH₃CN): 272 (30), 298 (30), 390 (6.4).

2.5.2. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_5)], E - 4a$

m.p. 229–231 °C (Found: C 84.43, H 5.41, Co 9.96; C₄₁H₃₁Co requires C 84.51, H 5.37, Co 10.11%). IR ν/cm^{-1} : $\nu(C=C)$ 1598, 1499 (CH₂Cl₂); $\nu(C=C)$ 1595, 1497 (KBr). ¹H NMR (CDCl₃): δ 7.32–7.10 (m, 25H, *Ph*, C₆H₅); 6.31 and 6.13 [2 × (d, ³J_{H,H} 16 Hz, 1H, CH=CH)]; 4.66 and 4.58 [2 × (m, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 136.6 (*C_i*, *C*₆H₅), 135.0, 127.7, 126.9 and 125.1 (C₄*Ph*₄); 127.8 and 122.6 (CH=CH); 127.3, 124.9 and 126.8 (CH, C₆H₅); 95.6 (*C_{ipso}*, C₅H₄), 84.8 and 81.1 (CH, C₅H₄); 75.6 (C₄Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 248 (43); 274 (47); 309 (sh, 31), 340 (sh, 27), 402 (sh, 7.7); (CH₃CN): 248 (38), 272 (42), 289 (30), 337 (sh, 24), 399 (sh, 7.0).

2.5.3. Z-[$Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_4 OMe - 4)$], Z-**4b**

m.p. 140–143 °C (Found: C 81.99, H 5.35, Co 9.38; C₄₂H₃₃OCo requires C 82.33, H 5.44, Co 9.62%). IR ν /cm⁻¹: ν (C=C) 1602, 1596, 1508, 1498 (KBr). ¹H NMR (CDCl₃): δ 7.51–7.13 (m, 20H, *Ph*); 7.10 and 6.74 [2 × (d, ³J_{H,H} 9 Hz, 2H, C₆H₄OMe)]; 6.19 and 5.55 [2 × (d, ³J_{H,H} 12 Hz, 1H, CH=CH)]; 4.54 (m, 4H, C₅H₄). ¹³C NMR (CDCl₃): δ 158.4 (C_p, C₆H₄OMe); 136.2, 128.9, 128.0, 126.2 (C₄*Ph*₄); 130.5 (C_i, C₆H₄OMe); 130.0 and 113.5 (C_{o/m}, C₆H₄OMe); 129.0 and 123.3 (CH=CH); 93.7 (C_{ipso}, C₅H₄); 84.3 and 83.0 (CH, C₅H₄); 75.2 (C₄Ph₄); 55.3 (CH₃). λ_{max} /nm (ϵ × 10⁻³/dm³mol⁻¹cm⁻¹) (CH₂Cl₂): 252 (41), 309 (30), 398 (sh, 5.6); (CH₃CN): 255 (39), 305 (30), 388 (sh, 6.8).

2.5.4. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_4 OMe - 4)], E - 4b$

m.p. 168–170 °C (Found: C 82.39, H 5.47, Co 9.55; $C_{42}H_{33}$ OCo requires C 82.33, H 5.44, Co 9.62%). IR ν/cm^{-1} : $\nu(C=C)$ 1596, 1512,

Table 1b

Crystal data for E-4f, E-4g, E-5.CHCl₃, Z-7.CH₂Cl₂, Z-8, and E,E-9.

| Compound | E- 4f | E- 4g | <i>E</i> - 5 .CHCl ₃ | <i>Z</i> - 7 .CH ₂ Cl ₂ | Z- 8 | E,E- 9 |
|---|------------------------------------|------------------------------------|---|--|--------------------------------|--|
| Empirical formula | C ₄₉ H ₃₅ Co | C ₅₁ H ₃₅ Co | C ₆₉ H ₅₁ Cl ₃ Co ₂ | C47 H37OCl2FeCo | C49H35N2CoFe | C ₈₀ H ₆₀ Co ₂ Fe |
| Formula weight | 682.70 | 706.72 | 1104.31 | 803.45 | 766.57 | 1194.99 |
| Temperature | 100(2) K | 293(2) K | 100(2) K | 293(2) K | 293(2) K | 100(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic | Orthorhombic | Triclinic |
| Space group | $P2_1/c$ | P-1 | P-1 | P21/n | P212121 | P-1 |
| Unit cell (Å) | a = 10.169(2) | a = 12.802(2) | a = 12.7089(8) | a = 10.0740(7) | a = 9.3446(10) | a = 10.4172(10) |
| dimensions | b = 28.520(6) | b = 17.526(3) | b = 14.2356(9) | b = 25.3200(17) | b = 10.6383(12) | b = 13.1619(13) |
| | c = 12.667(3) | c = 18.123(3) | c = 14.5400(9) | c = 14.7185(10) | c = 37.476(4) | c = 21.528(2) |
| (°) | $\alpha = 90$ | $\alpha = 103.485(3)$ | $\alpha = 91.055(1)$ | $\alpha = 90$ | $\alpha = 90$ | $\alpha = 92.338(2)$ |
| | $\beta = 108.248(4)$ | $\beta = 106.953(3)$ | $\beta = 98.951(1)$ | $\beta = 94.8980(10)$ | $\beta = 90$ | $\beta = 93.572(2)$ |
| | $\gamma = 90$ | $\gamma = 103.971(3)$ | $\gamma = 94.319(1)$ | $\gamma = 90$ | $\gamma = 90$ | $\gamma = 98.429(2)$ |
| Volume (Å ³) | 3488.8(12) | 3566.8(10) | 2589.9(3) | 3740.6(4) | 3725.5(7) | 2910.5(5) |
| Z | 4 | 4 | 2 | 4 | 4 | 2 |
| Density calculated | 1.300 | 1.316 | 1.416 | 1.427 | 1.367 | 1.364 |
| Absorption | $0.527 \ mm^{-1}$ | 0.518 mm^{-1} | 0.840 mm^{-1} | 1.011 mm^{-1} | 0.872 mm^{-1} | 0.857 mm^{-1} |
| E(000) | 1424 | 1/77 | 11/0 | 1656 | 159/ | 1240 |
| r(000) Crustal size (mm) | 1424 | 1472 0.40 × 0.20 × 0.05 | 1140 | 1000 | $1.00 \times 0.20 \times 0.02$ | 1240 |
| A range for data | 1 42 24 00° | 1.46 24.00 | 0.J0 × 0.40 × 0.20 1 // 20 50° | $0.80 \times 0.40 \times 0.50$ | 1.00 × 0.30 × 0.02 | 1.57 24.00° |
| collection | 1.45-24.00 . | 1.40-24.00 . | 1.44-28.36 . | 2.15-20.00 . | 1.55-24.00 . | 1.57-24.00 . |
| Index ranges | -11<=h<=11, | -14 <= h <= 14, | −17<=h<=16, | −12<=h<=12, | −10<=h<=10, | -11<=h<=11, |
| | −32<=k<=32, | −20<=k<=20, | -18 < = k < = 18, | −31<=k<=31, | −12<=k<=11, | −15<=k<=15, |
| | -14 <= l <= 14 | -20 <= l <= 20 | -19 <= l <= 19 | -18 <= l <= 18 | -42 <= l <= 42 | -24 <= l <= 24 |
| Reflections collected | 23413 | 47113 | 44661 | 64277 | 24477 | 20786 |
| Independent reflections | 5478 [R(int) = 0.0947] | 11192 [R(int) = 0.0306] | 12151 [R(int) = 0.0255] | 7349 [R(int) = 0.0213] | 5854 [R(int) = 0.0389] | 9073 [R(int) = 0.0479] |
| Completeness to $\theta = 24.0^{\circ}$ | 99.8% | 99.9% | 91.9% | 100.0% | 100.0% | 99.4% |
| Absorption | Multi-scan | Semi-empirical from | Semi-empirical from | Semi-empirical from | Semi-empirical from | Semi-empirical from |
| correction | Water Scall | equivalents | equivalents | equivalents | equivalents | equivalents |
| Max and min | 0 9948 and 0 5366 | 0.9746 and 0.8784 | 0.8500 and 0.6890 | 0.7513 and 0.6105 | 0.9828 and 0.7704 | 0.9831 and 0.5946 |
| transmission | 0.5540 and 0.5500 | 0.5740 and 0.5704 | | 0.7515 and 0.0105 | 0.5020 and 0.7704 | 0.5051 and 0.5540 |
| Refinement | Full-matrix least- | Full-matrix least- | Full-matrix least- | Full-matrix least- | Full-matrix least- | Full-matrix least- |
| method | squares on F ² | squares on F ² | squares on F ² | squares on F ² | squares on F ² | squares on F ² |
| Data/restraints/ | 5478/0/451 | 11192/198/1145 | 12151/0/871 | 7349/0/469 | 5854/0/478 | 9073/3/701 ^a |
| Coordinates of fit | 1 012 | 1 000 | 1.047 | 1.042 | 1.045 | 0.022 |
| on F ² | 1.012 | 1.080 | 1.047 | 1.042 | 1.045 | 0.932 |
| Final R indices | R1 = 0.0628, | R1 = 0.0452, | R1 = 0.0367, | R1 = 0.0453, | R1 = 0.0357, | R1 = 0.0425, |
| [I > 2sigma(I)] | wR2 = 0.1494 | wR2 = 0.1050 | wR2 = 0.0933 | wR2 = 0.1198 | wR2 = 0.0736 | wR2 = 0.0883 |
| R indices (all data) | R1 = 0.0991, | R1 = 0.0597, | R1 = 0.0405, | R1 = 0.0489, | R1 = 0.0433, | R1 = 0.0764, |
| | wR2 = 0.1711 | wR2 = 0.1128 | wR2 = 0.0958 | wR2 = 0.1233 | wR2 = 0.0764 | wR2 = 0.0985 |
| Largest diff. peak and hole (e.Å ⁻³) | 1.215 and -0.474 | 0.394 and -0.147 | 1.281 and -1.176 | 1.023 and -0.895 | 0.322 and -0.148 | 0.440 and -0.332 |
| | | | | | | |

1498 (KBr). ¹H NMR (CDCl₃): δ 7.51–7.13 (m, 20H, *Ph*); 6.99 and 6.80 [2 × (d, ³J_{H,H} 9 Hz, 2H, CH_{o/m} C₆H₄OMe)]; 6.36 and 6.07 [2 × (d, ³J_{H,H} 16 Hz, 1H, CH=CH)]; 4.73 and 4.67 [2 × (s, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 157.7 (*C_p*, C₆H₄OMe); 135.1, 127.7, 126.9, 125.1 (C₄*Ph*₄); 129.6 (*C_i*, C₆H₄OMe); 126.4 and 119.2 (CH=CH); 126.1 and 112.7 (*C_{o/m}*, C₆H₄OMe); 96.1 (*C_{ipso}*, C₅H₄); 83.4 and 79.7 (CH, C₅H₄); 75.5 (C₄Ph₄); 54.2 (CH₃). λ_{max}/mm ($\epsilon \times 10^{-3}/dm^{3}mol^{-1}cm^{-1}$) (CH₂Cl₂): 278 (47), 306 (sh, 33), 339 (sh, 29), 400 (sh, 8.3); (CH₃CN): 275 (45), 305 (sh, 32), 338 (sh, 28), 401 (sh, 8.0).

2.5.5. Z-[$Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4CH = CHC_6H_4Br - 4)$], Z-**4c**

m.p. 106–110 °C (Found: C 74.36, H 4.90, Br 12.37, Co 8.61; $C_{41}H_{30}BrCo$ requires C 74.44, H 4.57, Br 12.08, Co 8.91%). IR ν/cm^{-1} : ν (C=C) 1597, 1498, (CH₂Cl₂); ν (C=C), 1592, 1495, (KBr). ¹H NMR (CDCl₃): δ 7.39–7.19 (m, 20H, *Ph*); 7.32 and 6.99 [2 × (d, ³J_{H,H} 8 Hz, 2H, C₆H₄Br)]; 6.14 and 5.67 [2 × (d, ³J_{H,H} 12 Hz, 1H, CH=CH)]; 4.55 and 4.51 [2 × (m, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 137.2 (C_p , C₆H₄Br); 136.2, 129.0, 128.2, 126.5 (C₄*Ph*₄); 131.4 and 130.6 ($C_{0/m}$, C₆H₄Br); 127.9 and 125.7 (CH=CH); 93.0 (C_{ipso} , C₅H₄); 84.8 and 83.3 (CH, C₅H₄); 75.6 (C_4 Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 247 (50), 305 (34), 335 (sh, 26), 398 (7.1); (CH₃CN): 245 (50), 271 (44), 301 (34), 334 (sh, 25), 400 (7.4).

2.5.6. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_4 Br - 4)], E - 4c$

m.p. 182–184 °C (Found: C 73.75, H 4.68, Br 12.39, Co 8.58; C₄₁H₃₀BrCo requires C 74.44, H 4.57, Br 12.08, Co 8.91%). IR ν /cm⁻¹: ν (C=C) 1597, 1498, (CH₂Cl₂); ν (C=C), 1594, 1498, (KBr). ¹H NMR (CDCl₃): δ 7.41–7.14 (m, 20H, *Ph*); 7.35 and 6.88 [2 × (d, ³J_{H,H} 8 Hz, 2H, C₆H₄Br]); 6.29 and 6.19 [2 × (d, ³J_{H,H} 16 Hz, 1H, CH=CH)]; 4.75 and 4.70 [2 × (m, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 136.8 (*C_p*, C₆H₄Br); 136.2, 129.0, 128.2, 126.5 (C₄*Ph*₄); 131.6 and 127.7 (*C_{0/m}*, C₆H₄Br); 126.5 and 123.8 (CH=CH); 95.1 (*C_{ipso}*, C₅H₄); 85.1 and 81.3 (CH, C₅H₄); 75.8 (*C*₄Ph₄)..) λ_{max} /nm ($\epsilon \times 10^{-3}$ /dm³mol⁻¹cm⁻¹) (CH₂Cl₂): 247 (47), 277 (57), 305 (sh, 35), 344 (28), 404 (9.6); (CH₃CN): 249 (38), 275 (45), 301 (sh, 30), 342 (26), 404 (8.1).

2.5.7. Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₆H₄NO₂-4)], Z-**4d**

m.p. 195–197 °C (Found: C 78.32, H 4.85, N 2.22, Co 9.77; C₄₁H₃₀NO₂Co requires C 78.46, H 4.82, N 2.23, Co 9.39%). IR v/cm^{-1} : v(C=C) 1597, 1497, $v(NO_2)$ 1517,1342 (CH₂Cl₂); v(C=C) 1595, 1499, v

 $[RCH_2PPh_3]^{\dagger} \xrightarrow{base} RCHPPh_3 \xrightarrow{R'CHO} RCH=CHR' (1)$ $RCH_2P(O)(OEt)_2 \xrightarrow{base} [RCHP(O)(OEt)_2]^{\dagger} \xrightarrow{R'CHO} RCH=CHR (2)$

Scheme 1.

(NO₂) 1514,1340 (KBr). ¹H NMR (CDCl₃): δ 8.06 and 7.30 [2 × (d, ³J_{H,H} 8 Hz, 2H, C₆H₄NO₂)]; 7.40–7.17 (m, 20H, *Ph*); 6.22 and 5.85 [2 × (d, ³J_{H,H} 12 Hz, 1H, *CH*=*CH*)]; 4.64 and 4.55 [2 × (m, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 146.4 (*C_p*, C₆H₄NO₂); 145.4 (*C_i*, C₆H₄NO₂); 136.0, 129.0, 128.3, 126.7 (C₄*Ph*₄); 129.7 and 123.8 (*C_{0/m}*, C₆H₄NO₂); 128.8 and 126.6 (CH=*C*H); 92.2 (*C_{ipso}*, C₅H₄); 85.5 and 83.3 (CH, C₅H₄); 75.8 (C₄Ph₄). λ_{max} /nm ($\epsilon \times 10^{-3}$ /dm³mol⁻¹cm⁻¹) (CH₂Cl₂): 242 (43), 260 (44), 305 (sh, 34), 414 (9.9); (CH₃CN): 244 (39), 261 (41), 301 (sh, 31), 408 (9.2).

2.5.8. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_6 H_4 NO_2 - 4)], E - 4d$

m.p. 203–205 °C (Found: C 76.82, H 4.74, N 2.45, Co 9.01; C₄₁H₃₀NO₂Co requires C 78.46, H 4.82, N 2.23, Co 9.39%). IR ν/cm^{-1} :

ν(C=C) 1629, 1591, 1498, *ν*(NO₂) 1514, 1339 (CH₂Cl₂); *ν*(C=C) 1629, 1588, 1498 *ν*(NO₂) 1508, 1335 (KBr). ¹H NMR (CDCl₃): δ 8.15 and 7.13 [2 × (d, ³*J*_{HH} 9 Hz, 2H, C₆*H*₄NO₂)]; 7.44–7.18 (m, 20H, *Ph*); 6.43 and 6.38 [2 × (d, ³*J*_{HH} 16 Hz, 1H, CH=CH)]; 4.86 and 4.82 [2 × (s, 2H, C₅*H*₄)]. ¹³C NMR (CDCl₃): δ 146.2 (*C_p*, C₆H₄NO₂); 144.5 (*C_i*, C₆H₄NO₂); 135.9, 129.0, 128.3, 126.6 (C₄*Ph*₄); 128.6 and 125.0 (CH=CH); 126.3 and 124.2 (*C_{o/m}*, C₆H₄NO₂), 94.1 (*C_{ipso}*, C₅H₄); 85.9 and 81.8 (CH, C₅H₄); 76.1 (C₄Ph₄). λ_{max} /nm ($\epsilon \times 10^{-3}$ /dm³mol⁻¹cm⁻¹) (CH₂Cl₂): 243 (41), 260 (42), 307 (sh, 33), 429 (17); (CH₃CN): 243 (40), 269 (40), 304 (sh, 30), 421 (16).

2.5.9. Z-[$Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_{10}H_7 - 1)$], Z-**4e**

m.p. 163–165 °C (Found: C 85.76, H 5.77, Co 6.53; C₄₅H₃₃Co requires C 85.42, H 5.27, Co 9.31%). IR ν/cm^{-1} : $\nu(\text{C=C})$ 1596, 1498 (CH₂Cl₂); $\nu(\text{C=C})$ 1596, 1498 (KBr). ¹H NMR (CDCl₃): δ 8.27–7.09 (m, 27H, *Ph* & C₁₀H₇); 6.62 and 5.95 [2 × (d, J_{H,H} 12 Hz, 1H, CH=CH)]; 4.45 and 4.37 [2 × (t, J_{H,H} 2 Hz, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 135.0, 128.0, 127.0, 125.3 (C₄Ph₄); 134.4, (C_i, C₁₀H₇), 132.6 and 130.6 (Cq, C₁₀H₇); 128.2, 127.8, 127.4, 125.1, 124.6, 124.4 and 123.1 (CH, C₁₀H₇);



Scheme 2. (*i*) [RCH₂PPh₃]X/n-BuLi; **4** {R = (a) C₆H₅, (b) C₆H₄OMe-4, (c) C₆H₄Br-4, (d) C₆H₄NO₂-4, (e) 1-naphthyl} and **6** {R = Fe(η^5 -C₅H₅)(η^5 -C₅H₄-)}. (*ii*) *t*-BuLi then RCHO; **4** {R = (f) 9-anthyl, (g) 1-pyrenyl}, **5** {R = Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-)}. (*iii*) *t*-BuLi then 0.5 [Fe(η^5 -C₅H₄CHO)₂]. (*iv*) *n*-BuLi then 1 [Fe(η^5 -C₅H₄CHO)₂]. (*v*) CH₂(CN)₂/Et₃N.



Fig. 1. Molecular structure and atom labelling of *E*-[Co(η⁴-C₄Ph₄)(η⁵-C₅H₄CH=CHC₆H₅)], *E*-**4a**; thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.694(1); Co-C₅H₄(cent) 1.671(1); C(33)-C(34) 1.465(4); C(34)-C(35) 1.317(4); C(35)-C(36) 1.458(4). Selected bond angles (°) C(32)-C(33)-C(34) 127.6(3); C(29)-C(33)-C(34) 125.4(3); C(33)-C(34) -C(35) 126.1(3); C(34)-C(35) -C(36) 127.0(3); C₅H₄(cent)-Co-C₄Ph₄(cent) 178.12(2).

126.5 and 126.0 (CH=CH); 92.9 (C_{ipso} , C_5H_4); 83.7 and 83.3 (CH, C_5H_4); 75.1 (C_4Ph_4). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 311 (39), 335 (sh, 35); (CH₃CN): 309 (24), 332 sh (23).

2.5.10. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_{10}H_7 - 1)], E - 4e$

m.p. 176–178 °C (Found: C 83.98, H 5.49, Co 8.43; C₄₅H₃₃Co requires C 85.42, H 5.27, Co 9.31%). IR ν/cm^{-1} : $\nu(C=C)$ 1598, 1499 (CH₂Cl₂); $\nu(C=C)$ 1596, 1572, 1498, 1443 (KBr). ¹H NMR (CDCl₃): δ 7.95–6.98 (m, 27H, *Ph* & C₁₀H₇); 7.31 and 6.34 [2 × (d, J_{H,H} 16 Hz, 1H, CH=CH)]; 4.87 and 4.73 [2 × (m, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 135.5, 128.4, 127.6 and 125.8 (C₄*Ph*₄); 134.5, (C_i, C₁₀H₇); 133.1 and 130.5 (Cq, C₁₀H₇); 128.0, 126.9, 125.4, 125.3, 125.2, 123.5 and 122.8 (CH, C₁₀H₇), 125.4 and 124.1 (CH=CH); 95.8 (C_{ipso}, C₅H₄); 85.3 and 81.3 (CH, C₅H₄), 75.9 (C₄Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 228 (52), 301 (sh, 27), 347 (20); (CH₃CN): 297 (sh, 26), 346 (20).

2.5.11. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_{14}H_9 - 9)], E - 4f$

m.p. 178–182 °C (Found: C 85.26, H, 5.21, Co 8.16; C₄₉H₃₅Co requires C 86.20, H 5.17, Co 8.63%). IR ν /cm⁻¹: ν (C=C) 1602 (CH₂Cl₂); ν (C=C) 1594, 1499 (KBr). ¹H NMR (CDCl₃): δ 8.35–7.10 (m, 29H, *Ph* & C₁₄H₉); 7.42 and 6.32 [2 × (d, *J*_{H,H} 16 Hz, 1H, *CH*=*CH*)]; 5.03 and 4.76 [2 × (s, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 136.0, 128.8, 128.0 and 126.4 (C₄*Ph*₄); 132.9 (*C_i*, C₁₄H₉); 131.7, 128.5, 126.0, 125.4, 125.0 (*CH*, C₁₄H₉), 131.5, 129.3 (*Cq*, C₁₄H₉); 125.9 and 123.8 (*CH*=*CH*); 96.0 (*C_{ipso}*, C₅H₄); 85.3 and 80.5 (*CH*, C₅H₄); 75.5 (*C*₄Ph₄). λ max/ nm ($\epsilon \times 10^{-3}$ /dm³mol⁻¹cm⁻¹) (CH₂Cl₂): 258 (110), 408 (15); (CH₃CN): 255 (98), 407 (13).

2.5.12. $E - [Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 CH = CHC_{16}H_9 - 1)], E - 4g$

m.p. 199–201 °C (Found: C 86.73, H 4.80, Co 8.34; $C_{51}H_{35}$ Co requires C 86.67, H 4.99, Co 8.34%). IR ν/cm^{-1} : $\nu(C=C)$ 1602, 1499 (CH₂Cl₂); $\nu(C=C)$ (KBr). ¹H NMR (CDCl₃): δ 8.22–7.14 (m, 29H *Ph* & C₁₆H₉); 7.55 and 6.54 [2 × (d, J_{H,H} 16 Hz, 1H, CH=CH)]; 4.95 and 4.77 [2 × (s, 2H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 135.5, 128.4, 127.6 and 125.9 (C4*Ph*₄); 131.7 (*C_i*, C₁₆H₉); 131.2, 130.6, 129.9, 127.2 and 124.7 (*Cq*, C₁₆H₉); 127.1, 126.8, 126.5, 125.5, 124.7, 124.4, 123.0 and 122.9 (CH, C₁₆H₉); 125.6 and 124.0 (CH=CH); 96.0 (*C_{ipso}*, C₅H₄); 85.4 and 81.4 (CH, C₅H₄); 76.1 (*C*₄Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 243 (57), 280 (45), 380 (27), 405 (sh, 25); (CH₃CN): 231 (46), 279 (36), 376 (23).

2.5.13. $E - [Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4CH = CHC_5H_4 - \eta^5)Co(\eta^4 - C_4Ph_4)]$, E - 5m.p. 286–290 °C (Found: C 78.49, H 5.02, Co 11.32; $C_{68}H_{50}Co_2.CHCl_3$ requires C 78.75, H 4.87, Co 11.28%). IR ν/cm^{-1} : ν (C=C) 1602, 1498 (CH₂Cl₂); ν (C=C) 1596, 1498 (KBr). ¹H NMR (CDCl₃): δ 7.36–7.12 (m, 40H, *Ph*); 5.46 (s, 2H, *CH*=*CH*); 4.59 and 4.43 [2 × (m, 4H, C₅H₄)]. ¹³C NMR (CDCl₃): δ 136.4, 128.9, 128.0 and 126.2 (C₄*Ph*₄); 121.8 (CH=*C*H); 96.3 (C_{ipso} , C₅H₄); 84.0 and 80.7 (CH, C₅H₄); 75.3 (C₄Ph₄). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 247 (63), 265 (67), 305 (sh, 41), 350 (32), 412 (15); (CH₃CN): insoluble.

2.5.14. Z-[$Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Fe(\eta^5-C_5H_4CHO)$], Z-**7**

m.p. 168–171 °C (Found: C 70.19, H 4.68, Co 7.22; C₄₆H₃₅OFe-Co.CH₂Cl₂ requires C 70.26, H 4.64, Co 7.33, Fe 6.95%). IR ν /cm⁻¹: ν (C=O) 1681, 1664, ν (C=C) 1598, 1499 (CH₂Cl₂); ν (C=O) 1679, 1663, ν (C=C) 1594, 1498 (KBr). ¹H NMR (CDCl₃): δ 9.82 (s, 1H, CHO), 7.38–7.16 (m, 20H, *Ph*); 5.85 and 5.52 [2 × (d, ³J_{H,H} 12 Hz, 1H, CH=



Fig. 2. Molecular structure and atom labelling of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH= CHC₆H₄OMe-4)], *E*-**4b**; thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.692(1); Co-C₅H₄(cent) 1.678(1); C(29)-C (34) 1.457(3); C(34)-C(35) 1.328(3); C(35)-C(36); 1.466(3). Selected bond angles (°) C (33)-C(29)-C(34) 125.52(17); C(30)-C(29)-C(34) 127.96(17); C(29)-C(34)-C(35) 125.51 (19); C(34)-C(35)-C(36) 126.5(2); C₅H₄(cent)-Co-C₄Ph₄(cent) 178.15(2).



Fig. 3. Molecular structure and atom labelling of Molecule 1 of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₆H₄Br-4)], E-**4c**; thermal ellipsoids are drawn at the 50% probability level. Bond length and angle data for the three unique molecules. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.694(1), 1.690(1), 1.702(1); Co-C₅H₄(cent) 1.673(1), 1.674(1), 1.686(1); C(29)-C(34) 1.447(10), 1.457(11), 1.475(11); C(34)-C(35) 1.341(10), 1.324(10), 1.301(11); C(35)-C(36) 1.471(11), 1.455(11), 1.504(11). Selected bond angles (°)C(29)-C(33)-C(34) 125.1(7), 126.3(7), 122.9(7); C(32)-C(33)-C(34) 127.6(7), 127.4(7), 129.9(7); C(33)-C(34)-C(35) 127.3(7), 126.5(8), 126.5(8); C(34)-C(35)-C(36) 127.9(7), 127.5(8), 124.8(8); C₅H₄(cent)-Co-C₄Ph₄(cent) 178.28(7), 177.06(7), 177.49(6).

CH)]; 4.64 and 4.45 [2 × (t, ${}^{3}J_{\text{H,H}}$ 2 Hz, 2H, C₅H₄CHO)]; 4.60 and 4.57 [2 × (t, ${}^{3}J_{\text{H,H}}$ 2 Hz, 2H, C₅H₄Co)]; 4.30 and 4.22 [2 × (t, ${}^{3}J_{\text{H,H}}$ 2 Hz, 2H, C₅H₄Fe)]. 13 C NMR (CDCl₃): δ 193.5 (CHO); 136.1, 128.8, 127.9, 126.2 (C₄Ph₄); 124.8 and 123.9 (CH=CH); 93.5 (C_{ipso}, C₅H₄Co); 84.9 (C_{ipso}, C₅H₄Fe); 84.4 and 82.9 (CH, C₅H₄Co); 79.8 (C_{ipso}, C₅H₄CHO); 75.2 (C₄Ph₄); 74.4 and 70.6 (CH, C₅H₄CHO); 70.6 and 69.7 (CH, C₅H₄Fe). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^{3}mol^{-1}cm^{-1}$) (CH₂Cl₂): 238 (24), 262 (23), 300 (17), 404 (3.5); (CH₃CN): 238 (40), 262 (39), 299 (29), 411 (4.7).

2.5.15. Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe{ η^5 -C₅H₄CHC (CN)₂}], Z-**8**

m.p. 214–216 °C (Found: C 71.71, H 4.16, N 2.72; C₄₉H₃₅N₂Co-Fe.CH₂Cl₂ requires C 70.50, H 4.38, N 3.29%). IR ν/cm^{-1} : $\nu(\text{C}=\text{N})$ 2225, $\nu(\text{C}=\text{C})$ 1598, 1575, 1499 (CH₂Cl₂); $\nu(\text{C}=\text{N})$ 2219, $\nu(\text{C}=\text{C})$ 1594, 1574, 1498 (KBr). ¹H NMR (CDCl₃): δ 7.42 (s, 1H, *CH*=C(CN)₂); 7.39–7.19 (m, 20H, *Ph*); 5.71 and 5.64 [2 × (d, ³J_{H,H} 12 Hz, 1 H, *CH*=*CH*]; 4.81, 4.68, 4.66, 4.62, 4.36 and 4.24 [6 × (t, ³J_{H,H} 2 Hz, 2H, C₅H₄]]. ¹³C NMR (CDCl₃): δ 162.7 (*CH*=C(CN)₂); 136.1, 129.0, 128.2, 126.5 (*C*₄*Ph*₄); 125.4 and 123.9 (*CH*=CH); 115.4 and 114.5 (*C*=N); 93.3 (*C*_{ipso}, C₅H₄Co); 86.5 (*C*_{ipso}, C₅H₄Fe): 84.8 and 83.1 (*CH*, C₅H₄Co); 76.5 (*C*₄Ph₄); 75.2 and 72.7 (*CH*, C₅H₄Fe-CH=C(CN)₂); 75.1 (*C*_{ipso}, *C*₅H₄CH=C(CN)₂); 71.9 and 71.2 (*CH*, *C*₅H₄Fe). λ_{max}/mm ($\epsilon \times 10^{-3}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) (*C*H₂Cl₂): 243 (42), 262 (44), 307 (37), 405 (9.1), 536 (3.0); (CH₃CN): 239 (47), 260 (47), 303 sh (38), 392 (14), 528 (3.9).

2.5.16. $E_{,E} = [\{Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4CH = CHC_5H_4 - \eta^5\}_2Fe], E_{,E} = 9$

m.p. 225–228 °C (Found: C 80.01, H 5.18, Co 9.39, Fe 4.51; $C_{80}H_{60}Co_2Fe$ requires C 80.41, H 5.06, Co 9.86, Fe 4.67%). IR v/cm^{-1} : v(C=C) 1597, 1499 (CH₂Cl₂). ¹H NMR (CDCl₃): δ 7.43–7.18 (m, 40H, *Ph*); 6.07 and 5.82 [2 × (d, ³J_{H,H} 16 Hz, 2H, CH=CH)]; 4.64 and 4.61 [2 × (m, 4H, C₅H₄Co)]; 4.04 and 3.99 [2 × (t, ³J_{H,H} 2 Hz, 4H C₅H₄Fe)]. ¹³C NMR (CDCl₃): δ 136.2, 128.8, 127.9, and 126.1 (C₄*Ph*₄); 126.0 and 120.1 (CH=CH); 96.6 (*C_{ipso}*, C₅H₄Co); 84.4 (*C_{ipso}*, C₅H₄Fe); 84.1 and 80.3 (CH, C₅H₄Co); 75.2 (C₄Ph₄); 69.8 and 67.3 (CH, C₅H₄Fe). λ_{max}/nm ($\epsilon \times 10^{-3}/dm^3mol^{-1}cm^{-1}$) (CH₂Cl₂): 245 (87), 261 (85), 306 (59), 404 (18); (CH₃CN): insoluble.

2.6. Crystal structure determinations

The structures of *E*-4a, *E*-4b, *E*-4c, *E*-4d, *Z*-4e, *E*-4f, *E*-4g, *E*-5, *Z*-7, *Z*-8 and *E*,*E*-9 were determined by X-ray diffraction methods in the X-ray laboratory of University College Dublin. The structures of *E* and *Z*-6 have been reported previously [9] but various features are discussed for comparison purposes. The data were collected using a Bruker SMART APEX CCD area detector diffractometer and an X-ray tube utilising graphite-monochromated Mo Kα radiation



Fig. 4. Molecular structure and atom labelling of Molecule 1 of $E_{-}[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_6H_4NO_2-4)]$, *E*-**4d**; thermal ellipsoids are drawn at the 50% probability level. Bond length and angle data for the three unique molecules. Selected bond lengths (Å) Co-C_4Ph_4(cent) 1.696(1), 1.694(1), 1.696(1); Co-C_5H_4(cent) 1.680(1), 1.675 (1), 1.679(1); C(29)-C(34) 1.4615(14), 1.4527(13), 1.4483(13); C(34)-C(35) 1.3412(15), 1.3442(14); C(35)-C(36) 1.4653(15), 1.4589(13), 1.3442(14). Selected bond angles (°) C(33)-C(29)-C(34) 123.18(10), 123.95(9), 123.87(9); C(30)-C(29)-C(34) 129.27(10), 128.76(8), 128.75(9); C(29)-C(34)-C(35) 123.66(10), 124.07(9), 125.89(9); C (34)-C(35)-C(36) 1.25.75(10), 125.24(9), 124.62(9); C_5H_4(cent)-Co-C_4Ph_4(cent) 177.27 (1), 176.76 (1), 179.03(1).

 $(\lambda = 0.71073 \text{ Å})$. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS [18]. The structures were solved by direct methods using SHELXS-97 [19] and refined by full matrix least-squares on F^2 for all data using SHELXL-97 [19]. For compounds E-4a, E-4c, E-4f, E-4g, E-5, Z-7, Z-8 and E.E-9 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 E-4b, E-4d and Z-4e 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. Some calculations were carried out using ORTEX [20] and Mercury [21].

Crystal structure data are given in Tables 1a and 1b.

3. Results and discussion

Organic stilbenes may be prepared in many ways, but we have found that their ferrocenyl analogues are most conveniently obtained by routes based on the Wittig reaction [22,23] or its Horner–Wadsworth–Emmons (HWE) [24,25] modification (Scheme 1. Eqs. (1) and (2) respectively). In general, the Wittig reagent gives a mixture of *Z* and *E* alkenes. The Horner–Wadsworth–Emmons reagent is more reactive, but gives the *E* alkene only. Herein we extend this methodology to stilbenes containing the Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-) end group starting from either [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CHO)], **1**, or [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄PPh₃)][Cl], [**3**]Cl/[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄P(O)(OEt)₂], **2**, depending on circumstances.

The reactions carried out in the course of this work are shown in Scheme 2. The Wittig reaction (Scheme 1, Eq. (1)) was used to prepare **4a**, **4b**, **4c**, **4d**, **4e** and the previously reported **6** from [Co



Fig. 5. Molecular structure and atom labelling of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH= CHC₁₀H₇-1)], Z-**4e**; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.695(2); Co-C₅H₄(cent) 1.679(2); C(29)-C(34) 1.454 (3); C(34)-C(35) 1.326(3); C(35)-C(36) 1.484(3). Selected bond angles (°) C(33)-C(29)-C (34) 124.1(2); C(30)-C(29)-C(34) 129.0(2); C(29)-C(34)-C(35) 128.1(2); C(34)-C(35)-C (36) 125.5(2); C₅H₄(cent)-Co-C₄Ph₄(cent) 178.21(2).

 $(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CHO]/[RCH_2PPh_3]^+$, and **7** from $[Fe(\eta^5-C_5H_4CHO)_2]/[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH_2PPh_3]^+$ (1:1) using *n*-BuLi as a base. It always gave mixtures of *Z* and *E* isomers which were separated in most cases. However it failed to give **4f**, **4g** and **5** where R = 9-anthryl, 1-pyrenyl and Co($\eta^4-C_4Ph_4$)($\eta^5-C_5H_4-$) respectively. These and **9** were prepared by the HWE route (Scheme 1, Eq. (2)) from $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH_2P(O)(OEt)_2]$, **2**, and the



Fig. 6. Molecular structure and atom labelling of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₁₄H₉-9)], E-**4f**; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.678(1); Co-C₅H₄(cent) 1.665(1); C(33)-C(34) 1.447(6); C(34)-C(35) 1.323(6); C(35)-C(36) 1.481(6). Selected bond angles (°) C(32)-C(33)-C(34) 128.1(4); C(29)-C (33)-C(34) 124.6(4); C(33)-C(34)-C(35) 125.1(4); C(34)-C(35)-C(36) 124.4(4); C₅H₄(cent) -Co-C₄Ph₄(cent) 177.27(4).



Fig. 7. Molecular structure and atom labelling of $E_{-}[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHC_{16}H_9-1)]$, $E_{-}4g$; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) Co2-C_4Ph_4(cent) 1.689(2); Co2-C_5H_4(cent) 1.677(2); C(84)-C(85) 1.495(4); C(85)-C(86) 1.331(4); C(86)-C(87) 1.463(4). Selected bond angles (°) C(83)-C(84)-C(85) 126.1(3); C(80)-C(84)-C(85) 127.7(3); C(84)-C(85) -C(86) 126.0(3); C(85)-C(86) -C(87); 126.3(3); C_5H_4(cent) -Co2-C_4Ph_4(cent) 178.10(3).

appropriate RCHO using *t*-BuLi as the base, but only their *E* isomers were formed. However, the symmetrical E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Co(η^4 -C₄Ph₄)], **5**, was always a by-product of these reactions, and we have found that many RCH₂P(O)(OEt)₂/*t*-BuLi reagents give homodimers RCH = CHR in good yields when worked up in the absence of an aldehyde [26]. A similar reaction takes place with [RCH₂PPh₃]⁺, *t*-BuOK and acetophenone in polar aprotic solvents such as acetonitrile (R = aryl) [27].

The compounds **4**–**9** are air-stable crystalline solids soluble in many organic solvents though *E*-**5** and *E*,*E*-**9** are insoluble in acetonitrile. **4a**–**c**, *Z*-**4d**, **4e**–**g** and **5** are orange or orange brown, *E*-**4d** is red-brown, and **6**, **9**, **7** and **8** are red though the colour deepens markedly along that series.

3.1. Spectra

The IR spectra of **4–9** are dominated by the absorption bands due to the η^4 -C₄Ph₄ ligand, particularly those at ca. 1500 and 1600 cm⁻¹ due to the v(C=C) vibrations. There is little difference between them unless R contains an IR-active group. Thus the spectra of **4d** show absorption bands at ca. 1510 and 1340 cm⁻¹ due to their $v(NO_2)$ vibrations; for nitrobenzene these have frequencies of 1526 and 1347 cm^{-1} [27]. The aldehyde **7** shows two strong absorption bands in the v(CO) region at 1679 and 1663 cm⁻¹ whose frequencies are essentially identical with those found for its ferrocenyl analogue 1-formyl-1'-(ferrocenylethenyl)-ferrocene, 1679, 1663 cm⁻¹ in NaCl [28], and for 1,1'-diformyl-ferrocene, 1684, 1664 cm⁻¹ in KBr [29], but predictably are different from that reported for monosubstituted [$Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CHO)$], 1690 cm⁻¹ [30]. The dicyanovinyl **8** has a strong absorption band in the v(CN) region at 2225 cm⁻¹. At first glance this is significantly higher in energy than dicyanovinyl ferrocene $(2185, 2170 \text{ cm}^{-1})$ [31] and bears a closer resemblance to the 2225 cm^{-1} band for [Co(η^4 - C_4Ph_4 $\{\eta^5 - C_5H_4CH = C(CN)_2\}$ [12]. However, as with **7**, the presence of a 1'- conjugating group on the ferrocene lowers the stretching frequency of the 1- ring substituent, and thus the $v(C \equiv N)$ vibration for 8 compares favourably with that of 1,1'-bis(dicyanovinyl)-

ferrocene at 2220 cm⁻¹ [32]. These $v(C \equiv N)$ vibrations have lower frequencies than that observed for malononitrile, 2274 cm⁻¹ [12].

The ¹H NMR spectra of **4–9** show strong multiplets between δ 7.40 and δ 7.10 due to the protons of the η^4 -C₄Ph₄ ligands whilst the substituted cyclopentadienyl ligand give rise to a pair of triplets or a pair of broad resonances between δ 5.00 and δ 4.43. The protons of the CH=CH linker give rise to a singlet in the spectrum of 5 where the two end groups are identical, but all other compounds described have different end groups, the magnetic inequivalence generating two doublet signals. The observed coupling constants distinguish between the $E(J_{HH} = 16 \text{ Hz})$ and Z $(J_{HH} = 12 \text{ Hz})$ isomers of the stilbenes, and in all instances, coupling constant and X-ray data are consistent. In 4a, 4e, 4f and 4g resonances due to the aromatic end groups R either cannot be distinguished from those due to the C₄Ph₄ ligand or are weak, complicated multiplets. However, those due to the C_6H_4X -4 protons of 4b, 4c and 4d are readily identified as two characteristic doublets in each case with $J_{HH} = 8-9$ Hz whose chemical shifts depend on X and move downfield for OMe < Br < NO₂. Where R = Fe(η^{5} -C₅H₅) $(\eta^5-C_5H_4-)$ in **6** the C_5H_5 protons give rise to a singlet and the $\eta^5 C_5H_4$ to two triplets or broad resonances. In **7**, **8** and **9** the Fe(η^5 - C_5H_4 -)(η^5 - C_5H_4 -) moiety gives rise two pairs of triplets or broad bands. It is normally straight-forward to distinguish between Co $(\eta^5-C_5H_4-)$ and Fe $(\eta^5-C_5H_4-)$ signals as those due to the latter tend to lie upfield of those due to the former except in Fe(η^5 -C₅H₄-)(η^5 - C_5H_4X) complexes **7** and **8** where X is an electron-withdrawing CHO or CHC(CN)₂ substituent. These substituents themselves give rise to downfield singlets at δ 9.82, CHO, and δ 7.42, CHC(CN)₂.

It is also relatively straight-forward, by using homonuclear and correlation spectroscopy NMR techniques, comparisons with related compounds [7,12] and internal consistency, to assign peaks in the ¹³C NMR spectra of *E* and *Z* isomers of **4–9** to the C₄ ring and its attached Ph rings (1 and 4 resonance respectively), the C₅H₄Co ring (3 res), the CH=CH alkene carbons (2 res, but 1 in **5**), the terminal *p*-C₆H₄X (4 res) groups (**4b**-**4d**), and many of those of the polyaromatic end-groups of **4e**-**4g**. Rotation about the η^5 -C₅H₄-CH(=), (=)CH-C₆H₄X and (=)CH-anthryl bonds is fast on



Fig. 8. Molecular structure and atom labelling of Molecule 1 of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Co(η^4 -C₄Ph₄)], E-**5**; thermal ellipsoids are drawn at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation 1-*x*, 1-*y*, 2-*z*. Bond length and angle data for both unique molecules. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.687(1), 1.691 (1); Co-C₅H₄(cent) 1.672(1), 1.673(1); C(33)-C(34) 1.458(2), 1.464(2); C(34)-C(34)#1 1.339(3), 1.330(4); C(33)-C(34) 1.458(2), 1.464(2). Selected bond angles (°) C(32)-C(33)-C(34) 124.72(16), 124.23(17); C(29)-C(33)-C(34) 128.25(16), 128.70(17); C(34)#1-C(34)-C(33) 124.3(2), 124.7(2); C(34)#1-C(34)-C(33) 124.3(2), 124.7(2); C_5H₄(cent) 177.44(1), 177.59(1).

the NMR timescale. The resonances due to the $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)(4)$ or $Fe(\eta^5-C_5H_4-)(\eta^5-C_5H_4-)(3 \text{ or } 6)$ groups of **6** – **9** tend to lie upfield of those due to C_5H_4Co but move downfield when the electron-withdrawing CHO/CHC(CN)₂ are present.

The electronic spectra (300–900 nm) of 4a - 4c are similar to that of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_5)]$ with a weak absorption band at ca. 400 nm with a long tail [33]. Those of 4e - 4g also contain absorption bands which clearly arise from transitions within the naphthyl, anthryl or pyrenyl groups [7]. The spectra of Z and E isomers are very similar and are not greatly affected by the solvent. There appears to be limited or no electronic interactions between the $Co(\eta^4-C_4Ph_4)$ $(\eta^5-C_5H_4-)$ and R groups. Similar behaviour has been observed and discussed for related [Fe(η^5 -C₅H₅)(η^5 -C₅H₄CH=CHR)] compounds [7]. However, the spectra of 4d are different as they show a relatively strong absorption band at 408–429 nm. Its wavelength (λ) and intensity (ϵ) depends on the isomer and the former is solvent dependent i.e. for Z-4d λ = 414; 408 nm and ϵ = 9200; 9800 $dm^3mol^{-1}cm^{-1}$ in CH₂Cl₂; CH₃CN solutions, whilst for E-**4d** λ = 429; 421 nm and $\epsilon = 16,600$; 16,400 dm³mol⁻¹cm⁻¹ (CH₂Cl₂; CH₃CN). It appears that for these compounds there are some electronic interactions between $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4)$ (donor) and NO_2 (acceptor) groups. Similar low energy MLCT bands are observed in the spectra of the NLO-active *Z* and *E*-[Fe($\eta^5-C_5H_5$)($\eta^5-C_5H_4CH$ = CHCHC₆H₄NO₂-4)](λ = 480 and 496 nm respectively)[34,35]. Of the remaining compounds, **5**–**9**, only *Z*-**8**, *Z*-[Co($\eta^4-C_4Ph_4$)($\eta^5-C_5H_4CH$ =CHC₅H₄- η^5)Fe{ $\eta^5-C_5H_4CHC(CN)_2$], shows a weak, low energy absorption band in its electronic spectrum at λ = 536 nm (CH₂Cl₂ solution). Similar bands are observed at 536 nm for [Co($\eta^4-C_4Ph_4$){ $\eta^5-C_5H_4CH$ =C(CN)₂]] (CH₂Cl₂ solution) [12] and 521 nm for [Fe($\eta^5-C_5H_5$){ $\eta^5-C_5H_4CH$ =C(CN)₂]] (EtOH solution) [32].

3.2. Crystal and molecular structures

The structures of all 1-9 have been determined by X-ray diffraction techniques. Those of 1 - 3 have been reported previously [11,12] and will not be discussed further; those of *Z*-**6** and *E*-**6** have also been reported previously [9] but are included here for comparison with the closely related structures **7**–**9**. Crystal data are listed in Tables 1b and 1b, and molecular structures together with atom labelling are illustrated in Figs. 1–13.



Fig. 9. Molecular structure and atom labelling of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)], Z-**6**; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.691(1); Co-C₅H₄(cent) 1.674(1); Fe-C₅H₅(cent) 1.651(1); Fe-C₅H₄(cent) 1.644(1); C(29)-C(34) 1.464(2); C(34)-C(35) 1.338(2); C(35)-C(36) 1.470(2). Selected bond angles (°) C₅H₄(cent)-Fe-C₅H₅(cent) 179.18(2); C₅H₄(cent)-Co-C₄Ph₄(cent) 179.07(1). Taken from Ref [9].

In the cases of *E*-4c and *E*-4d, and *E*-5 and *E*,*E*-9 there are respectively three and two unique molecules in the asymmetric unit. Both molecules of 5 and 9 lie on special positions. In both molecules of 5 the centre of the C=C alkene double bond lies on an inversion centre, in 9, it is the central ferrocenyl iron atoms that sit on inversion centres. In molecule 2 of 9 the central di(cyclopentadienyl) ethene is disordered over two positions with refined occupancies of 0.600(6) and 0.400(6).

The structures of the $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR)]$ complexes **4**–**9** are broadly similar and conform to expectations. Their carbon frameworks contain a number of planes or quasiplanes which help describe them. The Co atom is sandwiched between two ca. planar $\eta^4-C_4Ph_4$ (the C₄ ring is Plane 1) and $\eta^5-C_5H_4$ - (Plane 2) ligands. The cyclopentadienyl ligand is σ -bonded to a CH—CH alkene linker which is, in turn, σ -bonded to R (C_{Co} -C(H)— C(H)-C_R constitutes Plane 3) where R is a ca. planar aromatic or polyaromatic (C₆H₄X-4, 1-naphthyl, 9-anthryl or 1-pyrenyl) or the cyclopentadienyl of a ferrocenyl group or second Co(η^4 -C₄Ph₄)(η^5 -C₅H₄) moiety (Plane 4). Plane 5 is the plane through the *para*phenyl -OCH₃ and -NO₂ substituent of **4b** and **4d**. Plane 6 is that of the second ring of these sandwich groups, (η^4 -C₄Ph₄)(η^5 -C₅H₄Y). The angles between these planes are listed in Table 2 together with the configurations of the Co(η^4 -C₄Ph₄)(η^5 -C₅H₄Y) and ferrocenyl groups. The C₅ and C₄ ligands on Co or the two C₅ ligands on Fe are effectively parallel with interplanar angles (1–2 or 3–6) of 0–4.9°. The dihedral between the η^5 -C₅H₄(Co) and alkene [C_{Co}-C(H)=C(H)-C_R] planes lie between 8.9 and 25.8° except for molecule 2 of *E*-**5** (1.9°) and for *Z*-**8** (46.6°). Progressing through the



Fig. 10. Molecular structure and atom labelling of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)], E-6; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.688(1); Co-C₅H₄(cent) 1.674(1); C(29)-C(34) 1.469(4); C(34)-C(35) 1.303(4); C(35)-C(36) 1.471(4); Fe-C₅H₅(cent) 1.648(1); Fe-C₅H₄(cent) 1.641 (1). Selected bond angles (°) C₅H₄(cent)-Fe-C₅H₅(cent) 178.20(2); C₅H₄(cent)-Co-C₄Ph₄(cent) 179.10(2). Taken from Ref [9].



Fig. 11. Molecular structure and atom labelling of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄- η^5)Fe(η^5 -C₅H₄-(Pd))], Z-7; thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.691(1); Co-C₅H₄(cent) 1.674(1); C(33)-C(34) 1.464(4); C(34)-C(35) 1.336(5); C(35)-C(36) 1.468(4); Fe-C₅H₄-CHO(cent) 1.638(1); Fe-C5H4-C=C (cent) 1.646(1). Selected bond angles (°) C₅H₄(cent)-Fe-C₅H₄(cent) 177.89(3); C₅H₄(cent)-Co-C₄Ph₄(cent) 176.68(2).



Fig. 12. Molecular structure and atom labelling of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe{ η^5 -C₅H₄CH=C(CN)₂}], Z-8; thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.691(1); Co-C₅H₄(cent) 1.673(1); C(33)-C(34) 1.466(5); C(34)-C(35) 1.332(4); C(35)-C(36) 1.457(5); Fe-C5H4-CH=C(CN)₂(cent) 1.651(1); Fe-C5H4-CE=C (cent) 1.651(1). Selected bond angles (°) C₅H₄(cent)-Fe-C₅H₄(cent) 175.61(3); C₅H₄(cent) 175.80(3), 175.61(3).



Fig. 13. Molecular structure and atom labelling of Molecule 1 of *E*,*E*-[{Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5]₂Fe], *E*,*E*-**9**; thermal ellipsoids are drawn at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation 2-*x*, 2-*y*, 1-*z*. Bond length and angle data for both unique molecules. Selected bond lengths (Å) Co-C₄Ph₄(cent) 1.685(1), 1.688(1); Co-C₅H₄(cent) 1.669(1), 1.701(2), 1.660(2); C(33)-C(34) 1.450(4), 1.484(6), 1.491(9); C(34)-C(35) 1.328(4), 1.337(8), 1.291(11); C(35)-C(36) 1.451(4), 1.427(6), 1.481(9); Fe-C₅H₄(cent) 1.664(2), 1.650(1), 1.649(1). Selected bond angles (°) C₅H₄(cent)-Fe-C₅H₄(cent) 180.0(3), 180.0; C₅H₄(cent)-Co-C₄Ph₄(cent) 177.64(3), 176.10(3), 173.12(3).

molecule, the angles between alkene (Plane 3) and aryl terminal or η^5 -C₅H₄ (Plane 4) range from an approximately coplanar 1.9° to near orthogonal 72.4°. They are smaller (1.9–18.6°) for the benzene compounds *E*-**4a**-**4d**, the pyrene derivative *E*-**4g**, and *E*-**5**. They tend to be smaller for *E* molecules than *Z*, and in the *Z* complexes Plane 3 has a pronounced helical distortion with angles of 3.6(3) – 6.8(6)° between its two constituent planes, C_{Co}-C-H and C-H-C_R.

The largest dihedrals are observed for *Z*-**4e** and *E*-**4f** and are clearly the result of steric crowding. For the *E*- structures the angles between Plane 2 and Plane 4 give an indication of the overall sandwich-aryl or sandwich—sandwich planarity (and hence possible conjugation through the alkene link), and lie between 21.4° and 44.1° The exceptions to this are the two molecules of *E*-**5** which lie on special crystallographic position (and thus have an

Table 2

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Interplane angles and conformation of the two \pi-ligands coordinated to Co or Fe in [Co(\eta^4-C<sub>4</sub>Ph<sub>4</sub>)(\eta^5-C<sub>5</sub>H<sub>4</sub>CH=CHR)] complexes.
```

| | Interplane | angles (°) ^a | | | | Conformatio | ns |
|---|------------|-------------------------|------|------------|------|-----------------------------------|-----------------------------------|
| R ^b | 1–2 | 2–3 | 3–4 | 4-5 or 4–6 | 2-4 | 1 vs 2 ^c | 4 vs 6 ^d |
| $C_6H_5(E-4a)$ | 2.7 | 22.2 | 12.2 | | 34.4 | e/c | |
| C ₆ H ₄ OMe-4 (<i>E</i> - 4b) | 1.8 | 22.0 | 16.1 | 4.16 | 38.1 | е | |
| C_6H_4Br-4 (<i>E</i> - 4c) | 2.3 | 13.6 | 10.9 | | 24.4 | е | |
| | 3.5 | 13.3 | 9.5 | | 22.7 | g | |
| | 1.8 | 9.4 | 12.3 | | 21.5 | f | |
| $C_6H_4NO_2-4(E-4d)$ | 3.3 | 17.2 | 9.7 | 10.9 | 26.6 | е | |
| | 2.2 | 14.5 | 14.8 | 5.3 | 29.3 | а | |
| | 0.8 | 14.1 | 18.8 | 4.0 | 32.9 | f | |
| 1-C ₁₀ H ₇ (Z- 4e) | 3.4 | 20.6 | 72.4 | | 68.5 | с | |
| $1-C_{14}H_9(E-4f)$ | 4.2 | 9.2 | 53.2 | | 44.1 | е | |
| 1-C ₁₆ H ₉ (<i>E</i> - 4g) | 1.9 | 8.9 | 18.1 | | 26.8 | f | |
| $Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 -) (E-5)$ | 3.1 | 10.2 | 10.2 | 3.1 | 0 | b | |
| | 3.3 | 1.9 | 1.9 | 3.3 | 0 | b | |
| $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)(Z-6)$ | 1.8 | 18.2 | 52.2 | 0.6 | 51.6 | е | e |
| $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)(E-6)$ | 1.2 | 13.8 | 11.1 | 2.6 | 2.9 | b | ес |
| Fe(η ⁵ -C ₅ H ₄ CHO)(η ⁵ -C ₅ H ₄ -) (Z- 7) | 3.3 | 25.8 | 44.3 | 2.3 | 50.6 | е | ес |
| $Fe{\eta^5-C_5H_4CH=C(CN)_2}(\eta^5-C_5H_4-)(Z-8)$ | 0.5 | 46.6 | 16.8 | 4.9 | 51.8 | е | ес |
| $Fe{\eta^5-C_5H_4CH=CH[Co]}(\eta^5-C_5H_{4^-}) (E,E-9)$ | 4.1 | 19.6 | 23.6 | 0 | 43.3 | С | st |

^a For definition of planes see text.

^b [Co] \equiv Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-).

^c The relative orientations of C₄ and C₅ ligands in the Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-) moiety. Nomenclature taken from ref. [33].

^d The relative orientations of two C₅ ligands in the Fe(η^{5} -C₅H₄Y)(η^{5} -C₅H₄-) molety; *ec* = eclipsed and *st* = staggered.

^e Approximately midway between eclipsed and staggered.



Fig. 14. Possible mesomers of M{ $\eta^5-C_5H_4CH=\!\!=\!\!C(X)Y$ derivatives, $M=Co(\eta^4-C_4Ph_4)$ or Fe($\eta^5-C_5H_5).$

inversion centre generated 0° dihedral) and the ferrocenyl E-6 (2.9°). The angles involving Plane 3 appear to be controlled by intra and inter-molecular non-bonding interactions, as they are in E and Z-stilbene where the angles between the equivalent of Planes 2 and 3 are respectively 1°/5° (X-ray diffraction) [36] and 43.2° (electron diffraction) [37], and electronic communication (or electron delocalization) between $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4-)$ and R groups across the C=C is probably limited in most instances. Calculations have shown that this is the case in various $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CH=$ CHR)] derivatives and it is reasonable to assume that the same is true here [8]. However, it is also probable that the $Co(\eta^4-C_4Ph_4)$ fragment has a greater steric influence than $Fe(\eta^5-C_5H_5)$ and consequently steric effects would be expected to be greater for complexes of the former than the latter even if electronic communication is anticipated. This is particular well-illustrated by the structures of E-[M(η^5 -C₅H₄CH=CHC₆H₄NO₂-4)]. When M = Fe $(\eta^5-C_5H_5)$ the $(\eta^5-C_5H_4CH=CHC_6H_4NO_2-4)$ portion of the molecule is close to planar [38], whereas for E-4d the dihedral angle between C_5H_4 and $C_6H_4NO_2$ planes averages 29.6° (Table 2). With the exception of Molecule 1 of *E*,*E*-**9**, the $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH]$ $CHC_5H_4-\eta^5)Fe(\eta^5-C_5H_5)$] derivatives tend to have their metal sandwich end groups on opposite sides of the C_{Co}-CH=CH-C_R plane.

The structures of the Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-) fragments are the same as those in related derivatives [9–12,33]. The η^4 -C₄Ph₄ ligands constitute a four-bladed propeller with the Ph planes inclined to the C₄ planes (interplanar angles = 18°–66.5°), whilst the CPh bonds point away from Co. The Co-centroid distances are 1.678(1) – 1.696(1) Å for the cyclobutadiene ligand and 1.665(1) – 1.680(1) Å for the cyclopentadienyl ligand. However, the Co-C distances are 1.95–2.00 Å and 2.03–2.10 Å respectively, and their C–C bond lengths are 1.45–1.48 Å and 1.38–1.44 Å respectively as compared with 1.303(4) – 1.343(4) Å for their ethylenic C=C bond lengths.

For the $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4C(34)H=C(35)H-R$ moiety the carbon atoms α [C(34)] and β [C(35)] to the cyclopentadienyl ring do not lie in its plane. On average C(34) is displaced from it by 0.0047 Å towards Co whilst for C(35) the displacement is -0.101 Å i.e. away from Co. However, in these complexes C(34) and C(35) are also β and α respectively to R where similar displacements are apparent. Such displacements can be attributed to the contribution that charge-separated fulvenic mesomers such as 2 make to the description of the electronic structures of these compounds (Fig. 14). However, this appears to be small as the displacement of $C\alpha$ is generally limited and variable, and is probably subordinate to steric effects except when substituents X and Y are electron accepting groups as in Z-7 and Z-8. Both of these compounds are derivatives of Z-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)], Z-**6**, but have their second η^5 -C₅H₅ ligand substituted by η^5 -C₅H₄CHO and η^5 -C₅H₄CH=C(CN)₂ respectively. For these their CH=O and CH=C(CN)₂ C α atoms are displaced from the C₅ plane towards Fe by 0.121 Å and 0.109 Å, whereas for the $(\eta^5-C_5H_4CH=$ $CHC_5H_4-\eta^5)Co(\eta^4-C_4Ph_4)$ ligands on Fe the comparable displacements are 0.058 and 0.092 Å, whilst in Z-6 it is -0.039 Å away from Fe. This suggests that the contribution made by mesomer 2 to Fe/ $(\eta^5-C_5H_4CH=X)$ bonding is much greater when X = 0 or $C(CN)_2$ than when X = CHR.

There is a further interesting feature of the structure and bonding in Z-8 which is not present in Z-7. The two C_5 ligands on Fe are eclipsed in both compounds but the CH=O and CH=CH substituents in Z-7 are not. However, in Z-8 the CH=C(CN)₂ and CH=CH substituents are eclipsed and the non-bonded C····C distances decrease $C(34) \cdots C(47) > C(36) \cdots C(41) > C(35) \cdots C$ (46) at 3.535(5), 3.411(5) and 3.325(5) Å compared with the interplane separation of 3.35 Å in graphite [39]. This suggests there is an attractive electronic interaction between the relatively electronrich CH=CH and electron-poor CH=C(CN)₂ ethylenic systems. This interaction cannot be negligible as it has a further consequence. In Z-6 and Z-7 the angles between the Planes 2 and 3 are 18.2 and 25.8° respectively whilst those between Planes 3 and 4 are 52.2 and 44.3°; in Z-8 they are 46.5 and 16.8° i.e. the introduction of the CH= $C(CN)_2$ substituents brings the $C_5H_4(Fe)$ and $C_iCH=CHC_i$ groups closer to co-planarity, but has the opposite effect on the $C_5H_4(Co)$ and C_iCH=CHC_i moieties. The totally eclipsed conformation has been found in the *E* ferrocenyl aldehyde $[Fe(\eta^5-C_5H_4CHO)(\eta^5 C_5H_4CH = CHFc-E$ which is disordered [28], [Fe(η^5 -C₅H₄CH = CHFc-*E*){ η^5 -C₅H₄CH=CH-C₅H₅N \rightarrow Cr(CO)₅-*E*}][28] where the nonbonded $C \cdot \cdot \cdot C$ distances equivalent to those for Z-8 are 3.720(8), 3.344(8) and 3.367(8) Å, [Fe(η⁵-C₅H₄CH=CH-C₆H₅Br-*E*)₂] [40], and l.l'-bis{(5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene) methyl}ferrocene, $Fe(\eta^5-C_5H_4CH=CS_2C_2S_2C_2H_4)_2$ [41].

On the other hand **9** is a *E,E* molecule. Both centrosymmetric molecules in the asymmetric unit adopt a strictly staggered conformation of the two $(\eta^5-C_5H_4CH=CHC_5H_4-\eta^5)Co(\eta^4-C_4Ph_4)$ ligands on Fe. This arrangement has also been observed for the

Table 3

Electrochemical data for $[\text{Co}(\eta^4\text{-}C_4\text{Ph}_4)(\eta^5\text{-}C_5\text{H}_4\text{CH}=\text{CHR})]^{a,b}$ and related compounds.

| Compound | | Oxidations Eo/V | |
|---------------|--|----------------------|--------------------------------------|
| | | [Co] | Other oxid ⁿ s |
| | $[Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_5)]$ | 0.98 | |
| Z- 4 a | C ₆ H ₅ | 0.94 | |
| E- 4 a | C ₆ H ₅ | 0.92 | |
| Z- 4b | C ₆ H ₄ OMe-4 | 0.89 | $1.15 (i_{pc}/i_{pa} 0.7)$ |
| E- 4b | C ₆ H ₄ OMe-4 | 0.87 | $1.14 (i_{\rm pc}/i_{\rm pa} 0.7)$ |
| Z- 4c | C_6H_4Br-4 | 0.96 | |
| E- 4c | C_6H_4Br-4 | 0.93 | |
| Z- 4d | $C_6H_4NO_2-4$ | 1.01 | |
| E- 4d | $C_6H_4NO_2-4$ | 0.99 | |
| E- 4e | $C_{10}H_7 - 1$ | 0.92 | |
| E- 4f | $C_{14}H_9-9$ | E _{pa} 0.89 | |
| E- 4g | $C_{16}H_9 - 1$ | 0.88 | $1.10 (i_{\rm pc}/i_{\rm pa} \ 0.8)$ |
| E- 5 | $Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 -)$ | 0.76, 0.90 | |
| Z-6 | $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)^c$ | 0.96 | 0.53 |
| E- 6 | $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)^c$ | 0.97 | 0.49 |
| Z- 7 | Fe (η ⁵ -C ₅ H ₄ CHO)(η ⁵ -C ₅ H ₅₄ -) | 0.89 | 0.76 |
| Z- 8 | $Fe{\eta^5-C_5H_4CHCH=C(CN)_2}(\eta^5-C_5H_{54}-)$ | 0.81 ^d | 0.81 ^d |
| E,E- 9 | $Fe{\eta^5-C_5H_4CHCH=CH[Co]}(\eta^5-C_5H_4-)$ | 0.88, 1.03 | 0.42 |
| E-10 | [Co]-CMe=CMe-[Co] ^e | 0.74, 0.88 | |
| 11 | [Co]-CMe=CPh ₂)] ^e | 0.90 | |
| | $[Co(\eta^4-C_4Me_4)(\eta^5-C_5H_5)]^f$ | 0.55 | |
| Z- 12 | [Et ₄ Co]-CH=CH-Fc ^g | 0.72 | 0.48 |
| E-12 | [Et ₄ Co]-CH=CH-Fc ^g | 0.69 | 0.46 |

 a 1 \times 10 $^{-3}$ M in CH_2Cl_2/0.1 M [Bu_4N][PF_6]/Pt/100mVs^{-1}/internal [Fe($\eta^5-C_5Me_5)_2$]^+/0 reference, [Fe($\eta^5-C_5H_5)_2$]^+/0 = 0.55 V [46].

^b $[Co] \equiv [Co(\eta^4 - C_4Ph_4)(\eta^5 - C_5H_4 -)]; [Et_4Co] \equiv [Co(\eta^4 - C_4Et_4)(\eta^5 - C_5H_4 -)]; Fc \equiv Fe (\eta^5 - C_5H_5)(\eta^5 - C_5H_4 -).$

^c Taken from ref. [9].

^d Two-electron process.

^e Preparation of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CMeC₅H₄- η^5)Co(η^4 -C₄Ph₄)] and [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CPh₂)] reported in ref. [10].

^f Data from ref. [45] (converted from original SCE ref.).

^g Preparation reported in ref. [43].



Fig. 15. Cyclic voltammogram of E-[Co]-CH=CH-[Co], 5 with internal [Fe(η^5 -C₅Me₅)₂] (= Fc*) chemical reference (100 mVs⁻¹, Pt, 0.1 M Bu₄NPF₆ in CH₂Cl₂, [FcH]^{0/+} = 0.55 V).

dipyridinyl [Fe(η^5 -C₅H₄CH=CH-C₅H₅N-*E*)₂], but in supramolecular aggregates with binaphthol it can adopt other conformations [42].

3.3. Electrochemistry

Electrochemical data for **4**–**9** in dichloromethane solution are summarised in Table 3 together with those for four compounds whose preparation, spectra and structure have been described elsewhere; E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CMeC₅H₄- η^5)Co(η^4 -C₄Ph₄)], E-**10** [10]; [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CPh₂], **11** [10]; Z-[Co(η^4 -C₄Et₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)], Z-**12** [43]; and E-[Co(η^4 -C₄Et₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)], E-**12** [43].

It has been reported previously that various $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4R)]$ [9,44], and $[Co(\eta^5-C_5H_4R)(\eta^4-C_4Me_4)]$ complexes [45] undergo a chemically reversible one-electron oxidation. For $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_5)]$ (=[Co]-H), this occurs at 0.98 V (*vs* [Fe($\eta^5-C_5Me_5)_2$]^{+/0} = 0.00 V) and is followed by a second irreversible oxidation process at higher anodic potential [44]. Similar behaviour is observed for $[Co(\eta^4-C_4Me_4)(\eta^5-C_5H_5)]$ with the initial oxidation occurring at 0.55 V [45]. All **4**–**12** display the couple associated with oxidation of the $Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4-)/Co(\eta^4-C_4Et_4)(\eta^5-C_5H_4-)$ moiety which appears to be chemically reversible with *i*_{pc}/*i*_{pa} \cong 1 except for the anthryl stilbene *E*-**4f** (see below).



Fig. 16. Cyclic voltammogram of *E*,*E*'-[{Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CH=CHC₅H₄- η^5 }]₂ Fe], *E*,*E*-**9**, with internal [Fe(η^5 -C₅Me₅)₂] (= Fc*) chemical reference (100 mVs⁻¹, Pt, 0.1 M Bu₄NPF₆ in CH₂Cl₂, [FcH]^{0/+} = 0.55 V).

Table 4

Spectroelectrochemical data for $[\text{Co}(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_4\text{CH}\text{=}\text{CHR})]^a$ and related compounds.

| Compound | | λ _{max} (nm) | | |
|---------------|--|-----------------------|----------|--|
| | | Monocation | Dication | |
| | $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_5)]$ | 653 | | |
| E- 4a | C ₆ H ₅ | 555, 955 | | |
| E- 4e | $C_{10}H_7 - 1$ | 628, 1109 | | |
| E- 4g | $C_{16}H_9 - 1$ | 655, 700, 1410 | | |
| E- 5 | $Co(\eta^4 - C_4 Ph_4)(\eta^5 - C_5 H_4 -)$ | 651, 1860 | 600 | |
| E- 6 | $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-)^b$ | 531, 1290 | | |
| E,E- 9 | $Fe\{\eta^{5}-C_{5}H_{4}CHCH=CH[Co]\}(\eta^{5}-C_{5}H_{4}-)$ | 541, 1290 | | |
| E-10 | [Co]-CMe=CMe-[Co] ^c | 649, 1800 | 593 | |
| 11 | [Co]-CMe=CPh ₂)] ^c | 570, 605, 1010 | | |
| E- 12 | [Et ₄ Co]-CH=CH-Fc ^d | 591, 1580 | | |

^a [Co] = [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄-)]; [Et₄Co] = [Co(η^4 -C₄Et₄)(η^5 -C₅H₄-)]; Fc = Fe (η^5 -C₅H₅)(η^5 -C₅H₄-).

^b Taken from ref. [9].

^c Preparation of E^{-} [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CMeC₅H₄- η^5)Co(η^4 -C₄Ph₄)] and [Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CPh₂)] reported in ref. [10].

^d Preparation reported in ref. [43].

Cyclic voltammetry performed on $E-[Co(\eta^4-C_4Ph_4)(\eta^5 C_5H_4CH = CHC_6H_5$], E-4a, shows an oxidation couple at 0.92 V. For Z-4a this appears at 0.94 V, and the anodic sweep of both isomers also shows an irreversible process at ca. 1.5 V. For other $[Co(n^4 C_4Ph_4$)(η^5 - C_5H_4CH =CHC₆H₄X-4)], there is also a ca. 0.2 V difference in E₀ between *E* and *Z* isomers, but when X is the electron-donating OMe group there is a cathodic shift of the redox couple to 0.87 V (E-4b) and 0.89 V (Z-4b) and a quasi-reversible oxidation of the methoxyphenyl group is observed at 1.14 V. On the other hand, when X is the electron-withdrawing NO₂ group there is a predictable anodic shift of the $[Co]^{+/0}$ redox couple to 0.99 V for *E*-4d and 1.01 V for Z-4d. The electrochemistry of the 1-naphthyl complex E-4e is very similar to that of E-4a; this is to be expected by comparisons with the electrochemistry of $[Fe(\eta^5-C_5H_5)(\eta^5-C_5$ $C_5H_4CH=CHR$] [7] and [Ni($\eta^5-C_5H_5$)C=C-R] [47] where R is an aryl group. The pyrenyl analogue E-4g exhibits both the reversible $[Co]^{+/0}$ and a quasi-reversible pyrenyl redox couple at 0.88 V and 1.10 V respectively. Uniquely, the anthracene derivative *E*-**4f** shows only an irreversible oxidation at 0.89 V; a companion cathodic feature occurs on the reverse sweep at 0.21 V. These may be associated with the anthryl group.

The closely related *E*-**5** and *E*-**10** with two redox centres display the classical Class II profile of two separate reversible one-electron oxidations ($\Delta E = 140 \text{ mV}$) suggesting interaction between the Co (η^4 -C₄Ph₄)(η^5 -C₅H₄-) moieties. For *E*-**5** these occur at 0.76 and 0.90 V (Fig. 15), whilst for its dimethylated analogue *E*-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CMeC₅H₄- η^5)Co(η^4 -C₄Ph₄)], *E*-**10**, they are found at 0.74, 0.88 V. The 20 mV shift is in the predicted cathodic direction.

The electrochemistry of Z- and E-**6** has been described previously [9] but is included for comparison purposes. The E- isomer displays two reversible oxidations at 0.49 and 0.97 V associated with the ferrocenyl and [Co] groups respectively. However in the case of the Z- isomer, following the second oxidation, a rapid cistrans isomerisation occurs and subsequent potential sweeps

resemble those of *E*-**6**. The corresponding tetraethylcyclobutadienylcobalt complexes *Z* and *E*-**12** [43] show similar behaviour, with the cobalt based oxidation predictably shifted cathodically by ~300 mV as a consequence of the superior electron donor ability of the η^4 -C₄Et₄ ligand compared with η^4 -C₄Ph₄.

E,*E*'-**9** undergoes three reversible oxidations (Fig. 16). The first, at 0.42 V, is associated with the ferrocenyl centre whilst the other two (0.88, 1.03 V) are due to the cobalt centres. These clearly communicate effectively through the extended ethenyl-ferrocenium-ethenyl linker, or perhaps more accurately, oxidation of the first cobalt centre affects the potential at which the second cobalt centre is oxidised. ΔE is 150 mV as compared with 140 mV for *E*-**5** with its shorter single C==C link.

3.4. Spectroelectrochemistry

Kudinov et al. have reported oxidation studies on various [Co $(\eta^4-C_4Me_4)(\eta^5-cyclopentadienyl)$ complexes and the results of DFT calculations for $[Co(\eta^4-C_4H_4)(\eta^5-C_5H_5)]$ [45]. One-electron oxidation in some instances gives rise to a relatively unstable monocation and the generation of cobaltocenium cation from consecutive elimination and disproportionation reactions [44,45]. Stable cations give rise to a new ferrocenium type metal-centred transition in the visible spectrum 576-680 nm [45]. Our results of preliminary spectroelectrochemical studies on a selection of the tetraphenylcyclobutadiene cobalt compounds are presented in Table 4. Oxidation in an OTTLE cell of the parent $[Co(\eta^4-C_4Ph_4)(\eta^5-$ C₅H₅) generates a new band at 653 nm ($\epsilon = 1300 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). The simple phenyl, naphthyl and pyrenyl $[Co(\eta^4-C_4Ph_4)(\eta^5-$ C₅H₄CH=CHR)] derivatives E-4a, E-4e and E-4g all show a similar relatively weak band 555-655 nm. Additionally a new band arises in the near infrared region of its spectrum associated with a ligandto-metal charge transfer (LMCT) from the aryl group to the oxidised cobalt centre. Their wavelengths, 955, 1110 and 1410 nm respectively, compare with 900, 956 and 1110 nm we reported for the analogous E-[Fe(η^5 -C₅H₅)(η^5 -C₅H₄-CH=CH-R)]⁺ species (R = phenyl, naphthy, pyrenyl) [7]. A similar band at 1010 nm is present in the spectrum of $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CMe=CPh_2]^+$, [11]⁺. The reversibility of the OTTLE spectra attest to the stability of these cations.

We have previously described the spectroelectrochemistry of the mixed ferrocene cobalt complex **6**. For *E*-**6** a one-electron oxidation in the OTTLE cell gives rise to a new charge transfer band at 1290 nm ($\epsilon = 2000 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) [7]. The same experiment performed on *Z*-**6** shows conclusively that a slow isomerisation to the sterically preferred *E* isomer takes place upon the first (ferrocenyl) oxidation. No isomerisation occurred when *Z*-**4a** was oxidised at $\text{E}^\circ[\text{Co}]^{+/0}$. The isomerisation of *Z*-**[6]**⁺ may proceed via an Fe-centred fulvene intermediate and rotation about the C α -C β bond (Scheme 3). OTTLE oxidation of the tetraethylcyclobutadiene complex **12**, results in a CT transition of much longer wavelength (lower energy), 1580 nm, but the same *Z* to *E* isomerisation of the oxidised species. The near-IR absorption bands of both *E*-**[6]**⁺ and *E*-**[12]**⁺ disappeared upon their oxidation to **[6]**²⁺ or **[12]**²⁺, providing additional support for their assignment to CT transitions.





Fig. 17. UV-vis OTTLE spectra of E-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CMe=CMeC₅H₄- η^5)Co(η^4 -C₄Ph₄)], E-**10**.

Oxidation of the *E*-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CR=CRC₅H₄- η^5)Co (η^4 -C₄Ph₄)] complexes *E*-**5** (R = H) and *E*-**10** (R = Me) at 0.75 V generates *E*-[Co(η^4 -C₄Ph₄)(η^5 -C₅H₄CR=CRC₅H₄- η^5)Co(η^4 -C₄Ph₄)]⁺ species with one [Co]⁺ acceptor and one neutral [Co] donor. This gives rise to a ferrocenium type transition at 650 nm and a broad, low energy intervalence charge transfer (IVCT) band at ca. 1800 nm/ 5550 cm⁻¹ (ϵ = ca. 1400 dm³mol⁻¹cm⁻¹) (Fig. 17). The IVCT interaction can be quantified from the electrochemical and OTTLE results by calculation of the Hush coupling term *V*_{AB} [48]. For *E*-**5** and **10**, *V*_{AB} = 0.07 eV. These values compare well with those for the IVCT band of *E*-[Fe(η^5 -C₅H₅)(η^5 -C₅H₄CH=CHC₅H₄- η^5)Fe(η^5 -C₅H₅)]⁺ where λ = 1750 nm (ϵ = 1200 dm³mol⁻¹cm⁻¹) and *V*_{AB} = 0.061 eV [49,50]. Upon oxidation of the second [Co] centre at 0.85 V the 1800 nm CT band is bleached and the [Co]⁺ transition shifts to shorter wavelength (Fig. 17).

The results for the OTTLE one-electron oxidation (at $E^{\circ}[Fe(\eta^{5}-C_{5}H_{5})_{2}]^{+/0}$) of $E,E'-\mathbf{9}$ to $E,E'-\mathbf{9}^{+}$ resemble those for the simpler compound E-**6**. The IVCT band appears at the same wavelength (1290 nm) but is of slightly higher intensity ($\epsilon = 3200 \text{ cf.} 2000 \text{ dm}^{3}\text{mol}^{-1}\text{cm}^{-1}$). The more highly oxidised $E,E'-[\mathbf{9}]^{2+}$ and $E,E'-[\mathbf{9}]^{3+}$ were not probed due to their instability on the OTTLE timescale.

4. Conclusions

Wittig or Horner–Wadsworth–Emmons methodology can be used to prepare organometallic stilbene analogues Z and E-[Co $(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR)$]. In most instances these show little or no evidence for electronic communication between the Co $(\eta^4-C_4Ph_4)(\eta^5-C_5H_4-) (\equiv [Co])$ and R groups except when R contains an electron-withdrawing substituent such as NO₂ or C(CN)₂. However, when the compounds are oxidised electrochemically the electronic spectra of the resultant $[Co(\eta^4-C_4Ph_4)(\eta^5-C_5H_4CH=CHR)]^+$ cations show low energy (950–1800 nm) absorption bands of low intensity which are attributed to $R \rightarrow [Co]$ or, when R is a ferrocenyl (\equiv Fc) derivative, $Fc^+ \leftarrow [Co]$ LMCT or IVCT transitions.

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Appendix A. Supplementary material

CCDC 801442–801452 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

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