Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 32.[1] One-electron Oxidation of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ (cot = cyclooctatetraene): Redox-induced Polycyclic Ring Transformations of the Resulting Dimer, and Crystal Structure of $[Co_2(\eta^4{:}\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ †

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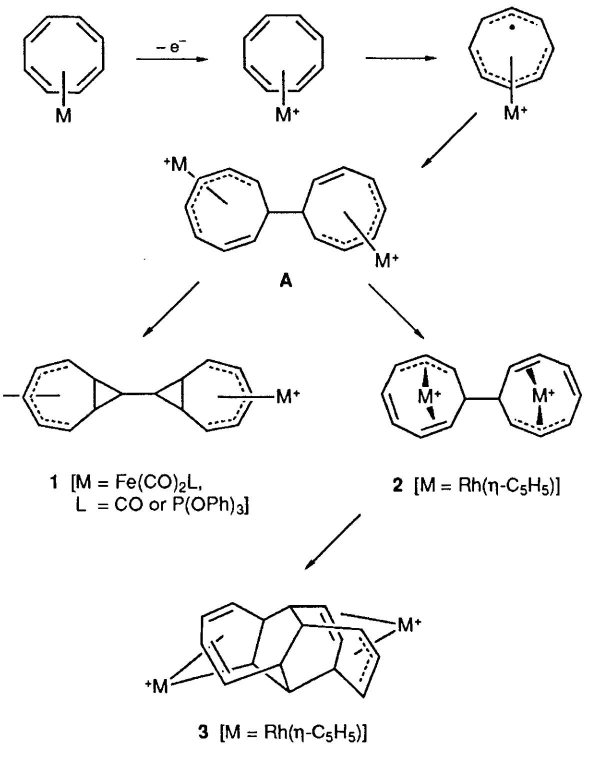
The complex $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ **4** (cot = cyclooctatetraene) undergoes irreversible one-electron oxidation in CH_2Cl_2 at a platinum electrode; chemical oxidation with $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ gives the dimeric dication $[Co_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **5** as a diastereomeric mixture. The reduction of **5** with two equivalents of $[Co(\eta\text{-}C_5H_5)_2]$ gives three asymmetric isomers $[Co_2(\sigma,\eta^3{:}\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **8**, $[Co_2(\sigma,\eta^3{:}\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **9** and $[Co_2(\eta^4{:}\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10**. Complex **8** is thermally isomerised to **10** which has been structurally characterised by a single crystal X-ray diffraction study. The two cobalt atoms, each carrying an $\eta\text{-}C_5Me_5$ ligand, are bonded to opposite sides of a tetracyclic $C_{16}H_{16}$ ligand which contains fused cyclooctatriene, cyclopentane, cyclopropane and cycloheptadiene rings; the cobalt atoms are bound *via* η^4-1,3- and η^4-1,5-diene interactions involving the C_7 and C_8 rings respectively. Complex **10** is oxidised by $[Fe(\eta\text{-}C_5H_5)_2]PF_6$, to give $[Co_2(\eta^2,\eta^3{:}\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **13**, and undergoes partial decomplexation with $Me_3NO{\cdot}2H_2O$ to yield the monometallic compound $[Co(\eta^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)]$ **15**. Stepwise rather than concerted mechanisms are proposed for the overall two-electron reduction of **5** and two-electron oxidation of **10**.

Our previous studies[2] of the oxidative dimerisation of co-ordinated cyclooctatetraene (cot) have shown there to be a marked dependence of the reactivity of the initial dimeric product **A** (Scheme 1) on the metal and its ancillary ligands. Thus, electrocyclic ring closure of **A** [M = $Fe(CO)_2L$, L = CO or $P(OPh)_3$] gives[3] $[Fe_2(CO)_4L_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})]^{2+}$ **1**, the precursor to a wide range of polycyclic hydrocarbon derivatives,[4] whereas **A** [M = $Rh(\eta\text{-}C_5H_5)$] undergoes[5] thermal isomerisation to $[Rh_2(\eta^2,\eta^3{:}\eta'^2,\eta'^3\text{-}C_{16}H_{16})(\eta\text{-}C_5H_5)_2]^{2+}$ **2** and then to the asymmetric species **3**; only an analogue of **2** is observed[6] on oxidation of $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$.

We now show that although the oxidation of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ **4** gives **A** [M = $Co(\eta\text{-}C_5Me_5)$], the reduction of this dication yields products the nature of which provides further insight into the mechanisms of the two-electron redox reactions of co-ordinated $C_{16}H_{16}$ ligands.

Results and Discussion

The electrochemistry of complex **4** has previously been studied in acetonitrile, cyclic voltammetry (CV) showing[7] an irreversible oxidation wave, and bulk electrolysis leading to decomposition with the (presumed) liberation of free cot. In CH_2Cl_2 the cyclic voltammogram of **4** is similar in that an irreversible oxidation wave is again observed [$(E_p)_{ox}$ = 0.10 V; scan rate (v) = 200 mV s^{-1}]. However, in this solvent the initial wave is accompanied by a series of product waves, in the potential range −0.6 to −1.4 V (Fig. 1), which imply the formation of well defined, cobalt-co-ordinated hydrocarbon complexes. This implication was borne out by the results of the chemical oxidation of **4**.



Scheme 1

The reaction between **4** and one equivalent of $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ (E° = 0.47 V) in CH_2Cl_2 gave, after addition of diethyl ether, an orange solid in good yield. Elemental analysis (Table 1) and the ^1H and ^{13}C NMR spectra (Table 2) showed the product

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical and mass spectrometric data for pentamethylcyclopentadienylcobalt complexes

				Analysis (%)[b]	
Complex	Yield (%)	Colour	M^{+} [a]	C	H
5 $[Co_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$	78	Orange	—	48.6 (48.8)	5.3 (5.2)
8 $[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$	41	Red	596	72.3 (72.5)	7.5 (7.8)
9 $[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$	10	Red	596	72.6 (72.5)	8.0 (7.8)
10 $[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$	76	Maroon	596	72.4 (72.5)	7.6 (7.8)
13 $[Co_2(\eta^2,\eta^3:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$	86	Orange	—	49.0 (48.8)	5.2 (5.2)
15 $[Co(\eta^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)]$	52	Brown	402	78.1 (77.6)	8.0 (7.8)

[a] By mass spectrometry. [b] Calculated values in parentheses.

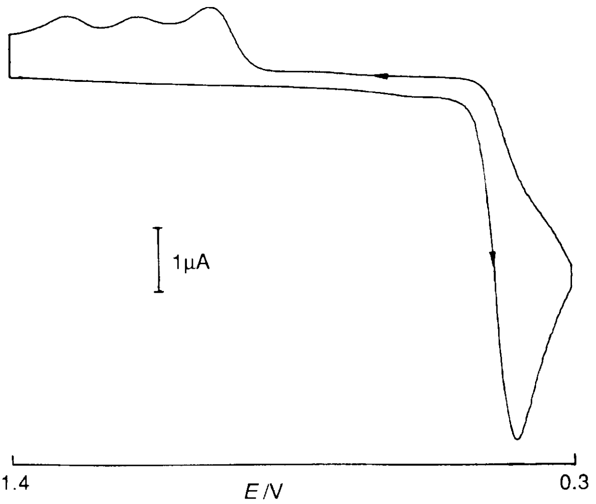
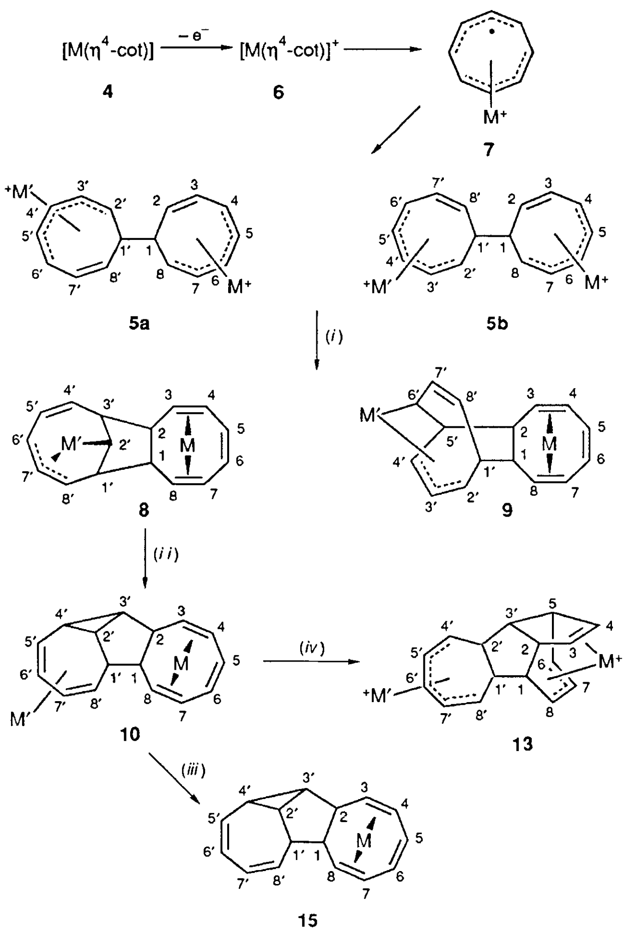


Fig. 1 Cyclic voltammogram of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ **4** from −1.4 to 0.3 V

to be the dicationic dimer $[Co_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **5** (Scheme 2) obtained as a mixture (*ca.* 6:5) of two diastereoisomers [due to the chiral centres at C(1) and C(1′)]; both the ^1H and ^{13}C NMR spectra show eight pairs of signals (a particular set of signals could not be assigned to a particular isomer).

By analogy with the mechanism previously proposed[2] for the oxidative dimerisation of co-ordinated cot complexes (Scheme 1) the primary product of the oxidation of **4** would be the 17-electron radical cation $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]^+$ **6** (Scheme 2). The formation of such a cation is supported[8] by molecular-orbital calculations on $[Co(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$, which are consistent with a predominantly metal-based highest-occupied molecular orbital. In addition, the photoelectron spectrum of $[Co(\eta^4\text{-cod})(\eta\text{-}C_5Me_4Et)]$ (cod = cycloocta-1,5-diene) indicated[9] ionisation from a metal-based orbital, and the cations $[Co(\eta^4\text{-cod})(\eta\text{-}C_5Me_5)]^+$[7] and $[Co(\eta^4\text{-}C_7H_{10})(\eta\text{-}C_5H_5)]^+$[10] were stable enough to give ESR spectra consistent with the presence of 17-electron metal centres. Cation **6** would then isomerise to the allyl-based radical $[Co(\eta^5\text{-}C_8H_8)(\eta\text{-}C_5Me_5)]^+$ **7**, allowing the cobalt atom to regain the 18-electron configuration, and C–C coupling would give dimer **5**.

The electrochemistry of $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ has provided[5] some evidence for a radical isomerisation process preceding dimerisation to **A** [M = $Rh(\eta\text{-}C_5H_5)$]. However, ^{60}Co γ-irradiation of $[Fe(CO)_2L(\eta^4\text{-cot})]$ [L = CO or $P(OPh)_3$] in $CFCl_3$ at 77 K leads to only one radical cation on electron loss; the ESR spectrum of this paramagnetic species suggested a semi-occupied molecular orbital with *ca.* 40:60 metal:C_8-ligand character.[11] Clearly the electron distribution in the radical intermediate(s) in the oxidative dimerisation reactions of co-ordinated cot complexes will be highly dependent on the metal and its ancillary ligands.



Scheme 2 M and M′ = $Co(\eta\text{-}C_5Me_5)$; (*i*) $2[Co(\eta\text{-}C_5H_5)_2]$, (*ii*) heat, (*iii*) Me_3NO, (*iv*) $2[Fe(\eta\text{-}C_5H_5)_2]^+$

It is also notable that **4** exists[12] in solution as a mixture of 1,3- and 1,5-bonded isomers (the iron cot complexes are exclusively 1,3-bound); the formation of a single dimeric oxidation product (albeit as diastereomers) provides some evidence for an allyl-like intermediate (*i.e.* **7**) in that such an intermediate can be formed readily from either 1,3- or 1,5-bonded 17-electron species.

As noted in Scheme 1, the first dimeric product of the oxidation of $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$, namely **A** [M = $Rh(\eta\text{-}C_5H_5)$], is isostructural with **5**. The dirhodium species undergoes[5] two sequential, thermal, isomerisations to **2** and **3**. By contrast, the cobalt complex **5** does not isomerise. However, it readily undergoes a two-electron reduction reaction to give products the nature of which has shed further light on the mechanism of redox-induced C–C bond forming reactions in binuclear species.

The cyclic voltammogram of **5** (Fig. 2) shows a diffusion-controlled, but irreversible, reduction peak at −0.84 V (scan rate 200 mV s^{-1}) together with two product reduction waves at *ca.* −1.08 and −1.27 V and a broad product oxidation wave at

Table 2 Proton and ^{13}C NMR spectroscopic data for Co(η-C$_5$Me$_5$) complexes[a]

Complex	δ(^{1}H)[b]	δ(^{13}C) (ppm)[c]
5	1.87 (15 H, s, C$_5$Me$_5$*), 1.90 (15 H, s, C$_5$Me$_5$), 3.49 (1 H, s, br, H^1), 3.55 (1 H, s, br, H^{1*}), 3.65 [^{1}H, dd, J(H^{2*}H^{3*}) 10.1, J(H^{2*}H^{1*}) 5.0, H^{2*}], 4.00 [1 H, dd, J(H^{2}H^3) 10.2, J(H^{2}H^1) 5.6 H^2], 4.22 [1 H, dd, J(H^{6*}H^{5*}) 10.5, J(H^{6*}H^{7*}) 6.5, H^{6*}], 4.26 [1 H, dd, J(H^{6}H^5) 10.3, J(H^{6}H^7) 6.7, H^6], 4.64 [1 H, dd, J(H^{3}H^2) 10.3, J(H^{3}H^4) 7.9, H^3], 4.69 [1 H, dd, J(H^{3*}H^{2*}) 10.1, J(H^{3*}H^{4*}) 7.8, H^{3*}], 4.90 (2 H, m, H^8, H^5), 5.00 [1 H, dd, J(H^{5*}H^{6*}) 9.7, J(H^{5*}H^{4*}) 7.3, H^{5*}], 5.25 [1 H, d, J(H^{8*}H^{7*}) 11.0, H^{8*}], 5.54 [1 H, dd, J(H^{7*}H^{6*}) 6.4, J(H^{7*}H^{8*}) 11.9, H^{7*}], 5.59 [1 H, dd, J(H^{7}H^6) 6.9, J(H^{7}H^8) 11.5, H^7], 6.46 [1 H, dd, J(H^{4}H^5) 7.4, J(H^{4}H^3) 7.4, H^4], 6.55 [1 H, dd, J(H^{4*}H^{5*}) 7.4, J(H^{4*}H^{3*}) 7.4, H^{4*}][d,e]	9.59 (C_5Me_5*), 9.64 (C_5Me_5), 44.13 (C^1), 44.37 (C^{1*}), 71.04 (C^{2*} or C^{6*}), 71.43, 71.92 (C^2, C^6), 72.24 (C^{2*} or C^{6*}), 94.08 ($C_5\mathrm{Me}_5$, $C_5\mathrm{Me}_5$*), 95.83 (C^3), 96.86 (C^{3*}), 101.89 (C^{5*}), 101.99 (C^5), 109.21 (C^{4*}), 109.63 (C^4), 125.29 (C^{8*}), 125.90 (C^8), 129.80 (C^{7*}), 131.18 (C^7)[d,e]
8	1.38 (15 H, s, C$_5$Me$_5$), 1.54 [1 H, dd, J(H$^{2'}$H$^{1'}$) 9.8, J(H$^{2'}$H$^{3'}$) 8.6, H$^{2'}$], 1.57 (15 H, s, C$_5$Me$_5$'), 2.47 (3 H, m, H^3, H^4, H$^{3'}$), 2.54 (2 H, m, H^7, H^8), 2.82 [1 H, ddd, J(H$^{1'}$H$^{2'}$) 10.4, J(H$^{1'}$H$^{8'}$) 7.6, J(H$^{1'}$H^1) 5.4, H$^{1'}$], 2.88 [1 H, ddd, J(H^{1}H^2) 11.1, J(H^{1}H$^{1'}$) 5.7, J(H^{1}H^8) 3.2, H^1], 3.06 [1 H, dd, J(H$^{7'}$H$^{6'}$) 9.8, J(H$^{7'}$H$^{8'}$) 7.8, H$^{7'}$], 3.31 [1 H, t, J(H$^{8'}$H$^{1'}$) = J(H$^{8'}$H$^{7'}$) 7.8, H$^{8'}$], 3.59 [1 H, dd, J(H^{2}H^1) 11.1, J(H^{2}H^3) 7.0, H^2], 3.83 [1 H, dd, J(H$^{6'}$H$^{7'}$) 9.6, J(H$^{6'}$H$^{5'}$) 7.7, H$^{6'}$], 5.90 [1 H, dd, J(H^{5}H^6) 6.6, J(H^{5}H^4) 2.7, H^5], 5.96 [1 H, dd, J(H$^{4'}$H$^{5'}$) 10.7, J(H$^{4'}$H$^{3'}$) 5.6, H$^{4'}$], 6.08 [1 H, ddd, J(H$^{5'}$H$^{4'}$) 10.4, J(H$^{5'}$H$^{6'}$) 7.8, H$^{5'}$], 6.12 [1 H, dd, J(H^{6}H^5) 6.4, J(H^{6}H^7) 2.0, H^6][f,g]	8.99 (C_5Me_5), 9.46 ($\mathrm{C}_5Me'_5$), 11.54, 51.07, 54.00, 57.11, 58.19, 58.83, 60.89, 71.07, 71.96, 74.26, 78.43, 90.47, 90.54, 92.00, 123.99, 132.32, 137.09, 139.07[f]
9	1.35 [1 H, J(H$^{6'}$H$^{5'}$) = J(H$^{6'}$H$^{7'}$) 7.9, H$^{6'}$], 1.39 (15 H, s, C$_5$Me$_5$), 1.58 (15 H, s, C$_5$Me$_5$'), 2.11 [1 H, dt, J(H$^{5'}$H$^{4'}$) = J(H$^{5'}$H$^{6'}$) 8.2, J(H$^{5'}$H^2) 1.1, H$^{5'}$], 2.14 [1 H, t, J(H$^{2'}$H$^{1'}$) = J(H$^{2'}$H$^{3'}$) 8.6, H$^{2'}$], 2.25 [1 H, dd, J(H^{7}H^8) 9.5, J(H^{7}H^6) 3.2, H^7], 2.42 [1 H, dd, J(H^{8}H^7) 9.5, J(H^{8}H^1) 6.1, H^8], 2.48 [1 H, dd, J(H^{4}H^3) 7.7, J(H^{4}H^5) 3.1, H^4], 2.75 (2 H, m, H$^{1'}$, H$^{3'}$), 2.87 (2 H, m, H^2, H^3), 2.99 [1 H, t, J(H$^{4'}$H$^{3'}$) = J(H$^{4'}$H$^{5'}$) 7.2, H$^{4'}$], 3.63 [1 H, dd, J(H^{1}H^2) 9.4, J(H^{1}H^8) 5.7, H^1], 5.79 [1 H, dd, J(H^{6}H^5) 6.6, J(H^{6}H^7) 3.2, H^6], 6.02 [1 H, dd, J(H^{5}H^6) 6.6, J(H^{5}H^4) 2.7, H^5], 6.13 [1 H, dd, J(H$^{7'}$H$^{8'}$) 10.1, J(H$^{7'}$H$^{6'}$) 7.5, H$^{7'}$], 6.22 [1 H, dd, J(H$^{8'}$H$^{7'}$) 10.1, J(H$^{8'}$H$^{1'}$) 7.2, H$^{8'}$][f,g]	8.97 (C_5Me_5), 9.27 (C_5Me_5'), 36.86, 37.00, 40.46, 41.13, 41.92, 50.69, 52.81, 60.45, 69.86, 71.99, 78.29, 81.62, 90.02, 90.43, 129.99, 134.20, 136.15, 137.10[f]
10	1.22 (1 H, m, H$^{2'}$), 1.40 (15 H, m, C$_5$Me$_5$, H$^{4'}$), 1.58 (1 H, m, H$^{3'}$), 1.71 (15 H, s, C$_5$Me$_5$'), 2.23 [1 H, t, J(H^{2}H^3) = J(H^{2}H$^{3'}$) 8.3, H^2], 2.43 [1 H, dd, J(H^{4}H^3) 8.9 J(H^{4}H^5) 2.6, H^4], 2.57 [1 H, dd, J(H^{7}H^8) 8.5, J(H^{7}H^6) 2.4, H^7], 2.63 [1 H, t, J(H$^{5'}$H$^{4'}$) = J(H$^{5'}$H$^{6'}$) 7.6, H$^{5'}$], 2.67 [1 H, t, J(H^{8}H^1) = J(H^{8}H^7) 8.3, H^8], 2.79 (2 H, m, H^3, H$^{8'}$), 3.33 (2 H, m, H^1, H$^{1'}$), 4.10 [1 H, ddd, J(H$^{6'}$H$^{5'}$) 7.8, J(H$^{6'}$H$^{7'}$) 4.2, J(H$^{6'}$H$^{8'}$) 1.7, H$^{6'}$], 4.61 [1 H, dd, J(H$^{7'}$H$^{8'}$) 6.7, J(H$^{7'}$H$^{6'}$) 4.3, H$^{7'}$], 5.69 [1 H, dd, J(H^{5}H^6) 6.5, J(H^{5}H^4) 2.8, H^5], 5.75 [1 H, dd, J(H^{6}H^5) 6.4, J(H^{6}H^7) 2.4, H^6][f,g]	9.03 (C_5Me_5), 10.22 (C_5Me_5'), 25.45, 39.62, 40.19, 44.18, 49.67, 59.94, 64.08, 70.77, 72.86, 75.02, 75.50, 79.70, 81.86, 82.27, 89.20, 92.12, 133.94, 136.69[f]
13	1.59 (1 H, m, H$^{3'}$), 1.74 (15 H, s, C$_5$Me$_5$), 1.85 (15 H, s, C$_5$Me$_5$'), 2.28 (1 H, m, H^2), 2.66 [1 H, dt, J(H$^{2'}$H$^{1'}$) = J(H$^{2'}$H$^{4'}$) 9.1, J(H$^{2'}$H$^{3'}$) 2.8, H$^{2'}$], 3.00 [1 H, t, J(H^{1}H^2) = J(H^{1}H^8) 7.0, H^1], 3.34 [1 H, t, J(H^{4}H^3) = J(H^{4}H^5) 4.3, H^4], 3.39 [1 H, dd, J (H$^{1'}$H$^{2'}$) 9.2, J(H$^{1'}$H$^{8'}$) 5.7, H$^{1'}$], 3.54 [1 H, dt, J(H^{5}H^6) = J(H^{5}H$^{3'}$) 7.5, J(H^{5}H^4) 4.3, H^5], 3.74 [1 H, dd, J(H^{7}H^8) 8.8, J(H^{7}H^6) 7.9, H^7], 4.11 [1 H, dd, J(H$^{8'}$H$^{7'}$) 9.6, J(H$^{8'}$H$^{1'}$) 5.6, H$^{8'}$], 4.43 [1 H, t, J(H$^{4'}$H$^{2'}$) = J(H$^{4'}$H$^{5'}$) 9.0, H$^{4'}$], 4.54 [1 H, t, J(H^{3}H^2) = J(H^{3}H^4) 4.2, H^3], 4.60 [1 H, t, J(H^{6}H^5) = J(H^{6}H^7) 7.7, H^6], 4.84 (2 H, m, H^8, H$^{7'}$), 4.98, [1 H, dd, J(H$^{5'}$H$^{4'}$) 8.4, J(H$^{5'}$H$^{6'}$) 6.4, H$^{5'}$], 6.55 [1 H, t, J(H$^{6'}$H$^{5'}$) = J(H$^{6'}$H$^{7'}$) 6.6, H$^{6'}$][e]	9.46, 9.81 (C_5Me_5, C_5Me_5'), 40.26, 44.03, 49.05, 54.05, 58.02, 60.21, 63.42, 72.02, 88.67, 88.97, 89.08, 92.18, 92.34, 98.12, 98.43, 100.23, 100.70, 102.42[e]
15	0.82 [1 H, dd, J(H$^{3'}$H$^{4'}$) 9.7, J(H$^{3'}$H$^{2'}$ 6.1, H$^{3'}$)], 1.04 [1 H, m, br, J(H$^{4'}$H$^{5'}$) 3.9, H$^{4'}$], 1.37 (15 H, s, C$_5$Me$_5$), 1.70 [1 H, q, J(H$^{2'}$H$^{1'}$) = J(H$^{2'}$H$^{3'}$) = J(H$^{2'}$H$^{4'}$) 6.4, H$^{2'}$] 2.46 [1 H, dd, J(H^{7}H^8) 9.2, J(H^{7}H^6) 2.6, H^7], 2.51 (1 H, m, H^3), 2.59 [1 H, dd, J(H^{4}H^3) 8.7, J(H^{4}H^5) 2.7, H^4], 2.71 [1 H, t, J(H^{8}H^1) = J(H^{8}H^7) 8.5, H^8], 2.90 [1 H, dt, J(H$^{1'}$H$^{8'}$) 8.4, J(H$^{1'}$H^1) 5.5, H$^{1'}$], 3.51 [1 H, ddd, J(H^{1}H^2) 11.4, J(H^{1}H^8) 8.4, J(H^{1}H$^{1'}$) 5.3, H^1], 3.63 [1 H, dd, J(H^{2}H^1) 11.5, J(H^{2}H^3) 7.7, H^2], 5.69 [1 H, dd, J(H^{6}H^5) 9.2, J(H^{6}H^7) 2.6, H^6], 5.79 [1 H, dd, J(H$^{7'}$H$^{8'}$) 11.4, J(H$^{7'}$H$^{6'}$) 5.7, H$^{7'}$], 5.83 [1 H, dd, J(H^{5}H^6) 9.2, J(H^{5}H^4) 2.7, H^5], 5.98 [1 H, dd, J(H$^{6'}$H$^{5'}$) 11.4, J(H$^{6'}$H$^{7'}$) 5.7, H$^{6'}$], 6.29 [1 H, dd, J(H$^{5'}$H$^{6'}$) 11.4, J(H$^{5'}$H$^{4'}$) 3.9, H$^{5'}$], 6.35 [1 H, dd, J(H$^{8'}$H$^{7'}$) 10.8, J(H$^{8'}$H$^{1'}$) 8.6, H$^{8'}$][f]	8.97 (C_5Me_5), 21.43, 24.53, 32.21, 47.86, 55.51, 65.54 (C^1, C^2, C$^{1'}$, C$^{2'}$, C$^{3'}$, C$^{4'}$), 71.69, 72.62, 75.07, 76.72 (C^3, C^4, C^7, C^8), 92.34 ($C_5\mathrm{Me}_5$), 126.01, 128.37, 134.20, 134.63, 136.17, 140.85 (C^5, C^6, C$^{5'}$, C$^{6'}$, C$^{7'}$, C$^{8'}$)[f]

[a] The atom numbering scheme for the NMR spectra of **8**–**10** is consistent with that for the X-ray structure of **10**. In order to show the relationship between **5** and **8** or **9**, all 16 ring carbons of **5** are numbered individually in Scheme 2. Note, however, that for the NMR spectra, C(1) ≡ C(1′), C(2) ≡ C(8′), C(3) ≡ C(7′), C(4) ≡ C(6′), C(5) ≡ C(5′), C(6) ≡ C(4′), C(7) ≡ C(3′) and C(8) ≡ C(2′). J values are in Hz. [b] 270 MHz spectra unless stated otherwise. [c] ^{1}H-decoupled, 67.9 MHz spectra. [d] The asterisk refers to the minor diastereomer. [e] In CD$_3$NO$_2$. [f] In C$_6$D$_6$. [g] 400 MHz spectrum.

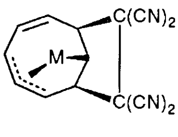
ca. −0.2 V. A comparison of the cyclic voltammograms of **4** and **5** (Figs. 1 and 2 respectively) clearly shows a qualitative correspondence in the potential range −0.6 to −1.4 V, implying that the products of the chemical and electrochemical oxidation of **4** are the same (or very similar).

We have been unable to determine (*e.g.*, by coulometry) the number of electrons involved in the electrochemical reduction of **5**. However, the chemical reduction requires *two* equivalents of the one-electron reductant [Co(η-C$_5$H$_5$)$_2$] for complete reaction in CH$_2$Cl$_2$. The reduction product, **B**, isolated in 85% yield *via* extraction into hexane and crystallisation, has a mass spectrum and elemental analysis (C and H) consistent with the formula [Co$_2$(C$_{16}$H$_{16}$)(η-C$_5$Me$_5$)$_2$], *i.e.* a dimer of **4**. However, NMR spectroscopy (^{1}H and ^{13}C) showed **B** to be a mixture of three isomers, each highly asymmetric, in the approximate ratio 3:1:trace.

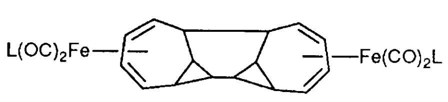
The mixture **B** could not be separated by column chromatography, the use of alumina or silica resulting in extensive decomposition. However, the two major components, **8** and **9**, were obtained isomerically pure as red crystals by fractional crystallisation from cooled hexane. Moreover, complex **8** is isomerised quantitatively in boiling hexane to **10** (isolated as maroon crystals) the trace component in mixture **B**. Thus, the three species have been individually characterised by elemental analysis and mass spectrometry (Table 1).

The ^{1}H NMR spectra of **8**–**10** are complex (Table 2) and were not assigned easily (see below). Attempts were therefore made to characterise the three isomers by X-ray crystallography; only crystals of **10** were successfully grown, from hexane at −78 °C.

The molecular structure of **10** was determined by a room-temperature single-crystal analysis and is illustrated in Fig. 3. Selected bond lengths and angles are given in Table 3. Compound **10** consists of two cobalt atoms, each carrying an η-C$_5$Me$_5$ ligand, bound to opposite sides of the C$_{16}$H$_{16}$ ligand by η^4-1,5- and η^4-1,3-diene interactions; the Co(1) $\cdots$ Co(2) distance is 7.116(2) Å. The tetracyclic C$_{16}$H$_{16}$ ligand contains fused C$_8$, C$_7$, C$_5$ and C$_3$ rings. The C$_8$ ring, a substituted cyclooctatriene, adopts a rather deep and slightly twisted tub conformation and is co-ordinated to Co(1) by two double bonds in the 1,5 arrangement observed for [Co(η^4-cyclooctatriene)(η-C_5H_5)].[13] The C_7 ring adopts a slightly twisted chair conformation and co-ordinates through an η^4-1,3-diene interaction to Co(2). The C_7 and C_8 rings are linked by fused cyclopropane and cyclopentane rings. The cyclopentane ring adopts a rather flattened envelope conformation, with C(1′) 0.24 Å from the mean plane through C(1), C(2), C(2′) and C(3′). The cyclopropane ring forms an isosceles triangle, with C(3′)–C(4′) rather longer than C(2′)–C(3′) and C(2′)–C(4′) [1.528(7) *vs.* 1.492(8) and 1.493(8) Å respectively]. This is consistent with delocalisation of the π system of the η^4-1,3-diene [C(5′)–(8′)] into the C(3′)–C(4′) σ* orbital, this interaction being favoured by the orientation of the cyclopropane ring[14] [the C_4 plane being nearly orthogonal to the C(3′)–C(4′) vector].



11 [M = Fe(CO)$_3$]



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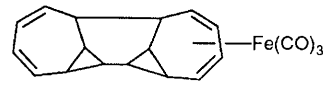


14

The X-ray structural study, together with ^{1}H-{^{1}H} decoupling experiments, allowed a full assignment to be made of the ^{1}H NMR spectrum of **10**. The chemical shifts of the η^4-1,3-diene protons [H(5′)–H(8′)] are similar to those of [Co(η^4-cyclohexa-1,3-diene)(η-C_5Me_5)][15] while the chemical shifts of the η^4-1,5-bonded cyclooctatriene ring [H(3), H(4), H(7), H(8)] are similar to those reported for [Co(η^4-cod)(η-C_5Me_5)][15] and the 1,5-bonded isomer of **4**.[12] The ^{13}C NMR spectrum, while not fully assigned, is also consistent with the solid-state structure in showing only two low-field signals (133.94 and 136.69 ppm), assigned to the carbon atoms of the unco-ordinated double bond, namely C(5) and C(6).

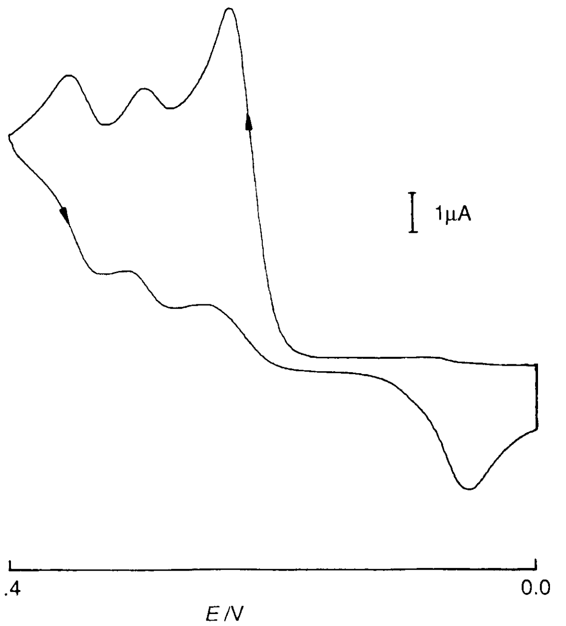


Fig. 2 Cyclic voltammogram of $[Co_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ from 0.0 to 1.4 V

The structures of **8** and **9** were deduced by comparing their 400 MHz ^{1}H NMR spectra with that of **10**, and with the aid of two-dimensional (^{1}H–^{1}H COSY) NMR spectroscopy. In each case the connectivity of the atoms of the $C_{16}H_{16}$ ligand was determined by considering both the one- and two-dimensional spectra; coupling constants were obtained from the one-dimensional spectrum (Table 2).

The structure proposed for **8** is shown in Scheme 2. The $C_{16}H_{16}$ ligand is tricyclic and is formed by joining two C_8 rings *via* bonds C(1)–C(1′) (the bond formed in the oxidative dimerisation of **4**) and C(2)–C(3′). The 1,2-disubstituted cyclooctatriene ring [C(1)–C(8)] is co-ordinated to one of the cobalt atoms in the same η^4-1,5-fashion observed for **10**. The other, 1,3-substituted C_8 ring [C(1′)–C(8′)] is σ,η^3-bound to the second cobalt atom in the manner found[16] for **11**, the 1,3-cyclo adduct of tetracyanoethylene with [Fe(CO)$_3$(η^4-cot)]. The ^{1}H–^{1}H couplings in the σ,η^3-bonded rings of **8** and **11**, and of the substituted derivatives[17] of **11**, are very similar. The σ-alkyl proton, H(2′) of **8**, shows couplings of 9.8 and 8.6 Hz to H(1′) and H(3′) respectively, similar to the couplings (11.5 and 6.5 Hz) of the analogous protons of **11** and implying that **8** also adopts the *exo* structure found for **11** [*i.e.* that bonds C(1)–C(1′) and C(2)–C(3′) are *exo* with respect to the metal atom bound to C(2′)].

The ^{13}C NMR spectrum of **8** is also consistent with the proposed structure; the high field shift of the signal due to the σ-bonded carbon atom [C(2′), 11.54 ppm], and its broadening by the strong interaction with the quadrupolar ^{59}Co nucleus ($I = \frac{7}{2}$), are particularly evident.

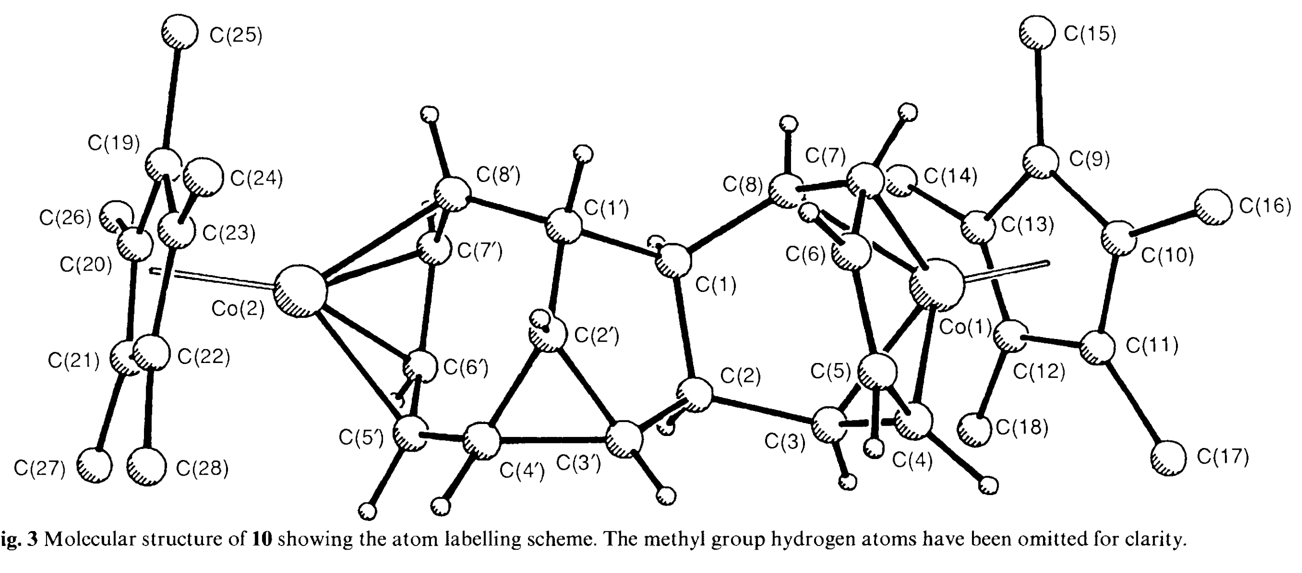
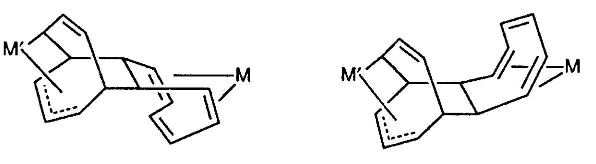


Fig. 3 Molecular structure of **10** showing the atom labelling scheme. The methyl group hydrogen atoms have been omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for compound **10**

Co(1)–C(3)	2.004(7)	C(7)–C(8)	1.415(7)	Co(1)–C(8)	2.003(7)	C(12)–C(13)	1.368(9)
Co(1)–C(7)	2.008(7)	C(9)–C(10)	1.412(9)	Co(1)–C(10)	2.083(7)	C(13)–C(14)	1.502(9)
Co(1)–C(9)	2.069(8)	C(9)–C(15)	1.512(10)	Co(1)–C(12)	2.116(7)	C(1′)–C(2′)	1.508(8)
Co(1)–C(11)	2.082(7)	C(10)–C(16)	1.513(8)	Co(2)–C(5′)	2.029(7)	C(2′)–C(4′)	1.493(8)
Co(1)–C(13)	2.097(8)	C(11)–C(17)	1.501(10)	Co(2)–C(7′)	1.950(7)	C(3′)–C(4′)	1.528(7)
Co(2)–C(6′)	1.982(7)	C(12)–C(18)	1.518(9)	Co(2)–C(19)	2.053(8)	C(4′)–C(5′)	1.474(7)
Co(2)–C(8′)	2.039(7)	C(1′)–C(8′)	1.531(7)	Co(2)–C(21)	2.083(7)	C(5′)–C(6′)	1.422(8)
Co(2)–C(20)	2.106(7)	C(2′)–C(3′)	1.492(8)	Co(2)–C(23)	2.028(7)	C(6′)–C(7′)	1.414(8)
Co(2)–C(22)	2.049(7)	C(19)–C(23)	1.421(9)	C(1)–C(2)	1.550(7)	C(7′)–C(8′)	1.417(7)
C(1)–C(8)	1.508(7)	C(20)–C(21)	1.414(8)	C(1)–C(1′)	1.571(7)	C(19)–C(20)	1.410(8)
C(2)–C(3′)	1.510(7)	C(21)–C(22)	1.423(7)	C(2)–C(3)	1.537(7)	C(19)–C(25)	1.531(10)
C(3)–C(4)	1.412(7)	C(22)–C(23)	1.403(8)	C(9)–C(13)	1.439(8)	C(20)–C(26)	1.487(8)
C(4)–C(5)	1.482(9)	C(23)–C(24)	1.513(8)	C(10)–C(11)	1.401(8)	C(21)–C(27)	1.509(8)
C(5)–C(6)	1.294(10)	Co(1)–C(4)	2.017(8)	C(11)–C(12)	1.431(8)	C(22)–C(28)	1.505(9)
C(6)–C(7)	1.469(9)						
C(3)–Co(1)–C(4)	41.1(2)	C(6)–C(7)–C(8)	124.6(5)	C(1′)–C(8′)–C(7′)	121.3(4)	Co(1)–C(7)–C(8)	69.2(3)
C(4)–Co(1)–C(7)	83.3(3)	Co(1)–C(8)–C(1)	113.7(3)	C(3)–Co(1)–C(7)	97.1(2)	Co(1)–C(8)–C(7)	69.5(3)
C(4)–Co(1)–C(8)	99.4(3)	C(1)–C(8)–C(7)	128.1(4)	C(3)–Co(1)–C(8)	84.8(2)	C(1)–C(1′)–C(2′)	105.1(4)
C(5′)–Co(2)–C(6′)	41.5(2)	C(2)–C(3′)–C(2′)	109.5(4)	C(7)–Co(1)–C(8)	41.3(2)	C(1)–C(1′)–C(8′)	112.5(4)
C(6′)–Co(2)–C(7′)	42.1(3)	C(2′)–C(3′)–C(4′)	59.2(3)	C(5′)–Co(2)–C(7′)	76.0(2)	C(2′)–C(1′)–C(8′)	115.7(4)
C(6′)–Co(2)–C(8′)	73.6(2)	C(2′)–C(4′)–C(3′)	59.2(3)	C(5′)–Co(2)–C(8′)	85.3(2)	C(1′)–C(2′)–C(3′)	109.8(4)
C(2)–C(1)–C(8)	112.2(4)	C(3′)–C(4′)–C(5′)	127.4(4)	C(7′)–Co(2)–C(8′)	41.5(2)	C(1′)–C(2′)–C(4′)	115.6(4)
C(2)–C(1)–C(1′)	107.0(4)	Co(2)–C(5′)–C(4′)	111.0(3)	C(8)–C(1)–C(1′)	115.0(4)	C(3′)–C(2′)–C(4′)	61.6(3)
Co(1)–C(3)–C(2)	114.2(4)	C(4′)–C(5′)–C(6′)	134.7(4)	C(1)–C(2)–C(3)	111.5(4)	C(2)–C(3′)–C(4′)	120.0(4)
C(2)–C(3)–C(4)	124.7(5)	Co(2)–C(6′)–C(5′)	71.0(3)	C(1)–C(2)–C(3′)	106.1(4)	C(2′)–C(4′)–C(5′)	125.2(5)
Co(1)–C(4)–C(3)	68.9(3)	C(5′)–C(6′)–C(7′)	119.5(4)	C(3)–C(2)–C(3′)	115.1(4)	Co(2)–C(5′)–C(6′)	67.5(3)
C(3)–C(4)–C(5)	122.1(5)	Co(2)–C(7′)–C(6′)	70.1(3)	Co(1)–C(3)–C(4)	69.9(3)	Co(2)–C(6′)–C(7′)	67.7(3)
C(5)–C(6)–C(7)	118.4(6)	C(6′)–C(7′)–C(8′)	116.7(4)	Co(1)–C(4)–C(5)	109.8(4)	Co(2)–C(7′)–C(8′)	72.6(3)
Co(1)–C(7)–C(6)	110.1(4)	Co(2)–C(8′)–C(1′)	123.9(4)	C(4)–C(5)–C(6)	117.4(6)	Co(2)–C(8′)–C(7′)	65.9(3)



9a **9b**

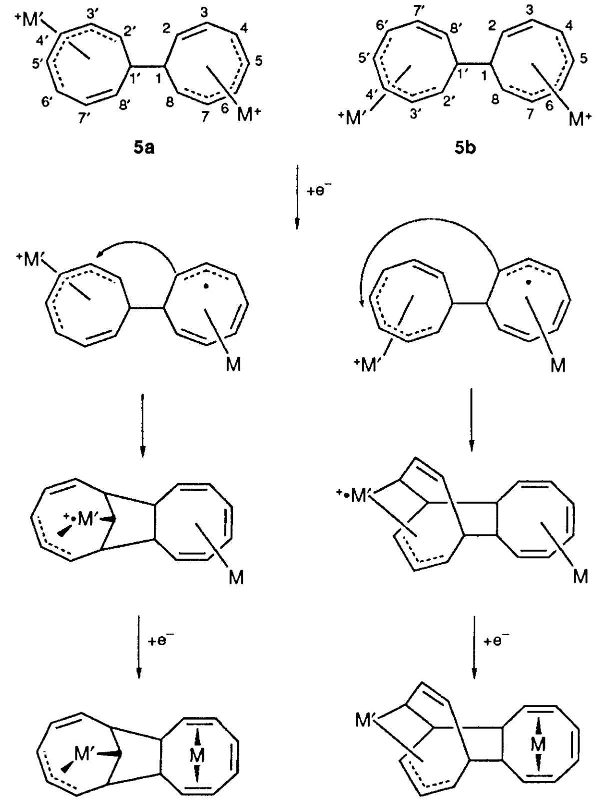
Fig. 4 Two possible conformations of complex **9**; M = M′ = Co(η-C_5Me_3)

The η^4-1,5-bound cyclooctatriene ring of **8** and **10** is also present in **9** (Scheme 2). The other C_8 ring, though co-ordinated to the second cobalt atom in a σ,η^3-mode similar to that of **8**, is linked to ring C(1)–C(8) *via* bonds at C(1′) [to C(1)] and C(5′) [to C(2)] rather than at C(1′) and C(3′). This mode of C_8 ring-linking generates two allyl fragments, one [C(2′)–C(3′)–C(4′)] π bound to M′ and the other [C(6′)–C(7′)–C(8′)] σ bonded to the same metal at C(6′); the NMR spectra are consistent with either of the two conformations (**9a** or **9b**; Fig. 4) for complex **9**.

The two-electron reduction of $[Fe_2(CO)_2L_2(\eta^5:\eta'5\text{-}C_{16}H_{16})]^{2+}$ **1** [L = CO or $P(OPh)_3$] gives [3] a single, symmetrical product $[Fe_2(CO)_2L_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})]$ **12**, *via* a proposed mechanism [2] involving concerted one-electron reduction of each of the two metal centres. Detachment of the terminal dienyl carbon atoms, after reduction, leads to regeneration of the 18-electron metal centres, and radical–radical coupling at the detached carbon termini yields the new C–C bond.

This type of concerted mechanism does not readily account for the formation of the highly asymmetric products **8** and **9** when dication **5** is similarly reduced by two electrons. Instead, a stepwise mechanism seems to be required. Various such mechanisms can be proposed but that shown in Scheme 3 has the advantage that **8** and **9** are formed from the diastereomers of **5** by the same basic processes.

The first step in the proposed mechanism involves the one-electron reduction of one of the metal centres of **5**. As in the case of iron, the reduced cobalt atom can regain the 18-electron configuration by detaching one carbon atom of the dienyl group, the odd electron remaining on an allyl fragment of the hydrocarbon ligand. The next step in the mechanism involves the attack of this carbon-based radical on the dienyl group attached to the second, cationic, cobalt centre, forming a second C–C bond between the two C_8 rings; alkyl radicals with π



8 **9**

Scheme 3 M and M′ = Co(η-C_5Me_5)

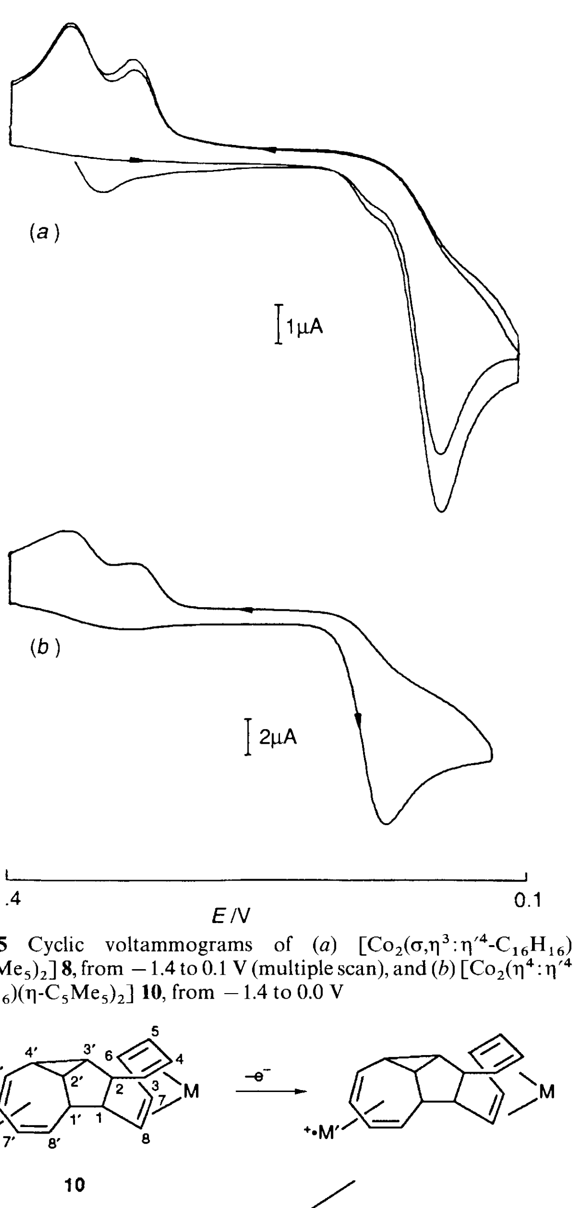
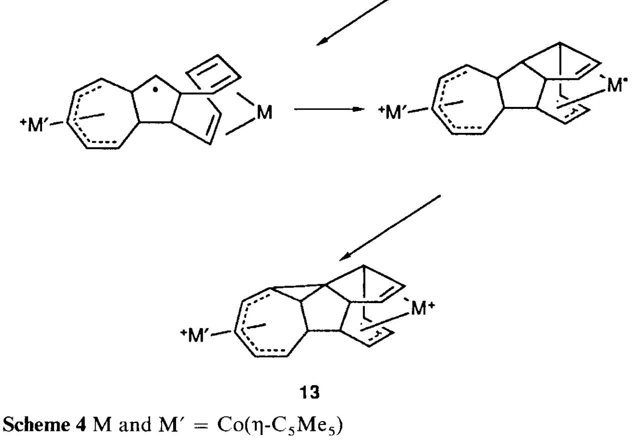


Fig. 5 Cyclic voltammograms of (*a*) $[Co_2(\sigma,\eta^3:\eta'^4-C_{16}H_{16})(\eta-C_5Me_5)_2]$ **8**, from −1.4 to 0.1 V (multiple scan), and (*b*) $[Co_2(\eta^4:\eta'^4-C_{16}H_{16})(\eta-C_5Me_5)_2]$ **10**, from −1.4 to 0.0 V



Scheme 4 M and M′ = $Co(\eta-C_5Me_5)$

character, *e.g.* allyls, are known [18] to act as nucleophiles towards aromatic substrates (though no reactions of such radicals with cationic 18-electron dienyl-metal complexes have been reported). The 17-electron centre generated at the second cobalt atom, by the C–C coupling step, is then reduced by the second equivalent of the one-electron reductant; isomerisation at the first cobalt atom, from the η^4-1,3- to the preferred η^4-1,5-arrangement, gives the final product **8** or **9**.

It seems likely that **8** is formed exclusively from diastereomer **5a**, *via* intramolecular attack (in the intermediate monocation) at C(3′), and that **9** results from **5b** *via* attack at C(5′). Molecular models show that these C–C bonds require the twisting of bond C(1)–C(1′) in order to allow partial eclipsing of the two C_8 rings and C–C coupling *exo* to the metals. Intramolecular radical attack at C(3′) in the one-electron reduction product of **5b** would result in a conformational isomer of **8** in which the C_8 rings were more nearly fully eclipsed. The structure determined for **10**, the thermal isomerisation product of **8**, militates against such a conformation.

One ambiguity in the proposed mechanism follows from the two possible conformations of **9** (*i.e.* **9a** and **9b**, Fig. 4). Attack at C(5′) of **5a** would give **9a** whereas the analogous reaction of **5b** would give **9b**; this ambiguity would be resolved by determining the X-ray structure of **9** but, as noted above, suitable crystals could not be grown.

The formation of the symmetrical complex **12** by reducing **1**, but of asymmetric redox products from the reduction of **5**, may result from concerted and stepwise mechanisms respectively. Alternatively, a stepwise mechanism may also apply in the iron chemistry with the different symmetry and steric requirements of dication **1** (*cf.* **5**) leading to the symmetric product. The difficulty in distinguishing between stepwise and concerted two-electron reduction mechanisms has been noted previously.[2]

The mechanism of the thermal isomerisation of **8** to **10** may either involve concerted electrocyclic ring closure mediated by a metal group [19] or the homolytic cleavage of the cobalt–carbon σ bond, Co(2)–C(2′) and subsequent sequential formation of C(2′)–C(4′) and C(5′)–Co(2). In **10** the Co(2) ··· C(2′) distance is extended to 3.344(7) Å, compared with the expected distance, *ca.* 2.15 Å, in **8**.[20] By whichever route **8** isomerises to **10** the driving force is presumably the formation of the η^4-1,3-diene unit in preference to the σ,η^3-arrangement.

The Reactions of Complex **10**.—The cyclic voltammograms of **8** and **10** [Figs. 5(*a*) and 5(*b*) respectively] are qualitatively similar. Each shows one irreversible oxidation wave, at −0.19 and −0.34 V respectively, which is coupled with two product waves at *ca.* −1.06 and −1.27 V. The oxidation wave of **8** is very similar in potential to that of the oxidation product wave in the cyclic voltammogram of **5** (Fig. 2), again suggesting a correspondence between the chemical and electrochemical redox behaviour of **5**. It is also notable that complex **10** is more readily oxidised than complex **8**, perhaps reflecting the different site of the first one-electron step, *i.e.* from a σ,η^3- or η^4-1,5-bound cobalt atom in **8** and from an η^4-1,3-cobalt atom in **10**. The two product reduction waves for both **8** and **10** occur at the same potentials as the product reduction waves observed in the cyclic voltammograms of **4** and **5**. The origin of these waves is discussed further below.

The chemical oxidation of **8** with two equivalents of $[Fe(\eta-C_5H_5)_2]PF_6$ in CH_2Cl_2 gave, after addition of diethyl ether, an orange solid which ^1H NMR spectroscopy showed to be a mixture of at least five species including the diastereomeric pair **5a** and **5b**. However, similar treatment of **10** gave a near quantitative yield of one product, namely $[Co_2(\eta^2,\eta^3:\eta'^5-C_{16}H_{16})(\eta-C_5Me_5)_2][PF_6]_2$ **13** (Tables 1 and 2, Scheme 2). (This product was also present in the mixture formed on oxidising **8**.)

The ^{13}C NMR spectrum of **13** (Table 2) shows 16 signals, due to the asymmetric $C_{16}H_{16}$ ligand, and inequivalent C_5Me_5 rings; further assignment was impossible. However, the ^1H COSY NMR spectrum allowed the bond connectivities, and hence the structure, of **13** to be determined. The dication is isomeric with **5** and contains a tetracyclic $C_{16}H_{16}$ ligand which is also different from that present in the asymmetric dirhodium complex **3** (Scheme 1). A seven-membered ring is co-ordinated to one cobalt atom as a 1,2-disubstituted η^5-cycloheptadienyl ligand, with the shifts and coupling constants of the dienyl fragment very similar to those observed for **5**. This ring is fused to the second part of the dication, *via* bonds C(1)–C(1′) and

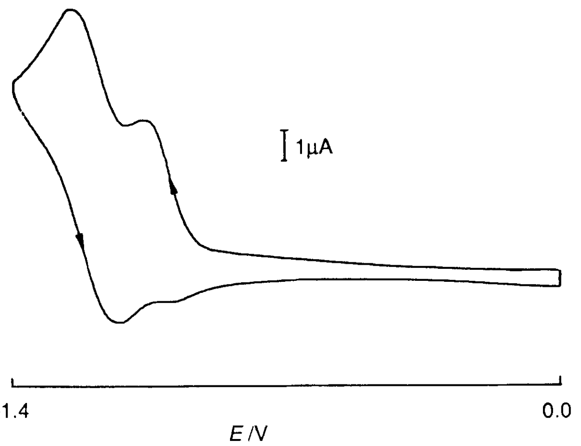


Fig. 6 Cyclic voltammogram of $[Co_2(\eta^2,\eta^3:\eta'^5-C_{16}H_{16})(\eta-C_5Me_5)_2][PF_6]_2$ **13** from 0.0 to −1.4 V

C(2′)–C(3′), to give a cyclopentane ring. The second metal atom is η^2,η^3-bonded to an eight-membered ring with the η^2-alkene moiety also part of a cyclopentene group.

On the basis of the structure suggested for **13**, and that determined for **10**, a mechanism for the oxidation of **10** may be proposed (Scheme 4); once again, two sequential one-electron transfer steps are preferred to a concerted two-electron process. Initial electron loss is from the η^4-cycloheptadiene-co-ordinated cobalt atom. As there are no free double bonds available for co-ordination of the resulting cationic 17-electron centre (*cf.* the oxidation of **4**, Scheme 2), the metal atom regains the 18-electron configuration *via* attack at the cyclopropane ring. (A similar process was proposed[4] for the oxidation of the dimeric iron complex **12**.) The cleavage of bond C(3′)–C(4′), the longest (and presumably weakest) bond of the three-membered ring, then allows the metal atom to co-ordinate to C(4′), generating a cationic η^5-dienylcobalt group; at the same time an odd electron is placed on C(3′). The tub conformation adopted by the cyclooctatriene ring bound to Co(1), in **10**, places the free double bond C(5)–C(6) close to C(3′) (Fig. 3); the non-bonded distance C(3′) ··· C(5) is only 2.986(9) Å. Thus radical attack of C(3′) on C(5) results in the formation of C(3′)–C(5). Finally, the bonding of the second cobalt atom to C(6) (the radical centre generated after the previous C–C coupling step) leads to a 19-electron centre which is oxidised, in the second one-electron step, to give **13**.

Alternative mechanisms seem less likely. Initial one-electron oxidation at the η^4-cyclooctatriene bound cobalt atom (which is not supported by the CV studies noted below) would lead to attack on double bond C(5)–C(6) by the 17-electron cobalt centre. Because the cyclooctatriene ring of **10** is very nearly symmetrical [the two saturated substituents at C(1) and C(2) are very similar], metal attack at C(6) is unlikely to be favoured over attack at C(5) and a mixture of products resulting from C(5)- and C(6)-based radicals might be expected. Similarly, a concerted process involving oxidation of both metal centres before C–C coupling would not be expected to distinguish between C(5) and C(6) (and, moreover, the two metal centres are unlikely to oxidise at the same potential, see below).

The cyclic voltammogram of **13** is shown in Fig. 6. Once again, two reduction waves at *ca.* −1.08 and −1.27 V are observed {*cf.* the product waves in the cyclic voltammogram of **10** [Fig. 5(*b*)]}. The potentials of these waves are compatible with the reduction of a dicationic species in that neutral complexes such as the 1,3- and 1,5-bonded isomers of **4** are reduced at much more negative potentials (*ca.* −2.0 V).[12] Thus, the occurrence of product waves in the potential range −1.0 to −1.4 V in the cyclic voltammograms of **8** and **10** is not surprising. It is not, however, clear why such waves occur in the cyclic voltammogram of **5** (and similarly in that of **4**) in that the chemical reduction of this dication leads to the isolation of only neutral species which would be expected to show reduction waves at *ca.* −2.0 V. One tentative explanation is that another dicationic species is formed catalytically in the initial stages of the reduction of **5**; it may be significant that **8**, formed by the chemical reduction of **5**, gives both **5** and **13** when oxidised with ferrocenium ion.

The $C_{16}H_{16}$ ligand of **10** is a new isomer of the known cyclooctatetraene dimers.[3,4,21] Attempts were therefore made to isolate the free ligand after metal decomplexation. The reactions of **10** with CO, PPh_3 or 2,2′-bipyridyl did not result in loss of the $Co(\eta-C_5Me_5)$ group, and iodine gave an orange solid containing the dication **13**. Treatment of **10** with $[NH_4]_2[Ce(NO_3)_6]$ in methanol resulted in complete decomposition. However, the reaction of **10** with an excess of $Me_3NO \cdot 2H_2O$ in benzene under reflux, a method successfully used[3] to obtain the pentacyclic isomer of $C_{16}H_{16}$ found in **14**, gave a brown solid, **15**, whose colour was similar to that of $[Co(\eta^4\text{-cot})(\eta-C_5Me_5)]$ **4**. Indeed, microanalysis and mass spectrometry (Table 1) confirmed that only one $Co(\eta-C_5Me_5)$ group had been removed from **10**, *i.e.* that the product was $[Co(\eta^4-C_{16}H_{16})(\eta-C_5Me_5)]$ **15** (Scheme 2).

The ^1H NMR spectrum of **15** revealed that the cobalt atom η^4-bound to the cycloheptadiene ring in **10** is decomplexed selectively; the signals due to the cobalt-co-ordinated cyclooctatriene ring are almost identical to those observed for **10**. The selective loss described reflects the previously observed[8] preference of $Co(\eta-C_5R_5)$ (R = H or Me) for co-ordination of non-conjugated rather than conjugated dienes, in direct contrast to the related $Fe(CO)_3$ fragment.[22] The unco-ordinated part of the $C_{16}H_{16}$ ligand of **15** shows signals with coupling constants and chemical shifts in close agreement with those of the uncomplexed part of $[Fe(CO)_3(\eta^4-C_{16}H_{16})]$ **14** (and the corresponding free hydrocarbon).[3] Thus, compound **15** has the same $C_{16}H_{16}$ framework found in **10**.

The cyclic voltammogram of **15** shows a diffusion-controlled oxidation wave which is reversible at a scan rate of 2 V s^{-1}. The potential of this wave $[(E_p)_{ox} = 0.26$ V, 200 mV $s^{-1}]$ is considerably more positive than that of **10** $[(E_p)_{ox} = -0.34$ V$]$ in spite of the presence of the same $C_{16}H_{16}$ ligand. Assuming there to be little electronic interaction between the two metal centres, it is likely that the oxidation of the cyclooctatriene bound cobalt of **10** would occur at *ca.* 0.26 V. We conclude, therefore, that oxidation of **10** occurs first at the cycloheptadiene-metal centre, as proposed in the stepwise mechanism shown in Scheme 4.

Brief attempts were made to react **15** with sources of metal groups, such as $Fe(CO)_3$ and $Rh(\eta-C_5H_5)$, capable of binding to the unco-ordinated cycloheptadiene fragment; the oxidation of the resulting heterobimetallic species, for example $[(OC)_3Fe(\eta^4:\eta'^4-C_{16}H_{16})Co(\eta-C_5Me_5)]$ would be expected to occur at the electron rich $Co(\eta-C_5Me_5)$ site, *i.e.* at the cyclooctatriene fragment rather than the cycloheptadiene group of **10**. Unfortunately no such mixed-metal species could be prepared.

Conclusion

The oxidative dimerisation of $[Co(\eta^4\text{-cot})(\eta-C_5Me_5)]$ yields a diastereomeric pair of complexes which are precursors to a range of highly asymmetric $C_{16}H_{16}$ derivatives. The observation of such asymmetric species suggests that overall two-electron processes occur *via* stepwise single-electron reactions. More detailed electrochemical studies may shed further light on the mechanisms involved.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled and deoxygenated solvents. The complexes $[Co(\eta^4\text{-cot})(\eta-C_5Me_5)]$,[15,23] $[Fe(\eta-C_5H_5)_2]PF_6$[24] and

Table 4 Atomic coordinates (× 10^4) for compound **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	1158(1)	−2466(1)	−621(1)	C(18)	2238(4)	−4736(5)	−457(6)
Co(2)	4122(1)	1026(1)	2036(1)	C(1′)	2383(3)	204(3)	823(3)
C(1)	2247(3)	−1016(3)	604(3)	C(2′)	2830(3)	657(4)	138(3)
C(2)	2862(3)	−1289(3)	−35(3)	C(3′)	3157(3)	−232(4)	−343(3)
C(3)	2399(3)	−2046(4)	−733(3)	C(4′)	3812(3)	473(4)	251(3)
C(4)	1786(4)	−1720(5)	−1457(3)	C(5′)	4393(3)	154(4)	1049(3)
C(5)	1466(4)	−601(5)	−1577(4)	C(6′)	4281(3)	−494(4)	1749(3)
C(6)	957(4)	−250(5)	1076(4)	C(7′)	3529(3)	−338(4)	2135(3)
C(7)	707(3)	−989(4)	−448(3)	C(8′)	2873(3)	389(4)	1732(3)
C(8)	1293(3)	−1347(4)	286(3)	C(19)	3964(4)	2197(4)	2891(4)
C(9)	83(3)	−3313(4)	−342(4)	C(20)	4787(3)	1688(4)	3184(3)
C(10)	61(3)	−3343(4)	−1223(3)	C(21)	5307(3)	1803(4)	2546(3)
C(11)	850(3)	−3834(4)	−1355(3)	C(22)	4799(3)	2403(4)	1873(3)
C(12)	1359(3)	−4140(4)	−551(4)	C(23)	3962(3)	2635(4)	2075(4)
C(13)	897(4)	−3823(4)	60(3)	C(24)	3244(4)	3303(4)	1541(5)
C(14)	1152(6)	−4023(6)	995(4)	C(25)	3186(4)	2296(6)	3369(4)
C(15)	−659(4)	−2882(6)	72(5)	C(26)	5075(5)	1126(6)	4005(3)
C(16)	−668(4)	−2917(6)	−1911(4)	C(27)	6254(3)	1420(5)	2594(4)
C(17)	1064(5)	−4107(5)	−2205(4)	C(28)	5130(4)	2735(5)	1085(3)

$[Co(\eta\text{-}C_5H_5)_2]$[25] were prepared by published methods. The ^1H and ^{13}C NMR spectra were recorded on JEOL GX 270 or GX 400 spectrometers and calibrated against $SiMe_4$ as an internal reference. Two-dimensional NMR spectroscopy employed the COSY-45 pulse sequence. Mass spectra were recorded on an AEI MS 902 spectrometer. Cyclic voltammetry was carried out as described previously.[26] Under the conditions used, $E°$ for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.09 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Syntheses.—$[Co_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **5**. To a stirred solution of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ **4** (0.35 g, 1.17 mmol) in CH_2Cl_2 (40 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ (0.38 g, 1.16 mmol). After 10 min the orange solution was filtered and evaporated to low volume. Addition of diethyl ether (200 cm^3) gave the product as an orange solid, yield 0.40 g (78%).

The complex dissolves in polar solvents such as CH_2Cl_2 and acetone to give orange solutions which decompose in air.

$[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **8**. A stirred solution of $[Co_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **5** (0.45 g, 0.51 mmol) in CH_2Cl_2 (100 cm^3) was treated with $[Co(\eta\text{-}C_5H_5)_2]$ (0.19 g, 1.00 mmol). After 5 min the solvent was removed *in vacuo* and the residue extracted with hexane (2 × 30 cm^3). The extract was filtered, evaporated to minimum volume and cooled to −10 °C for 18 h to give the product as red crystals. Concentration and cooling of the mother-liquors afforded more product, total yield 0.12 g (41%).

The complex slowly isomerises when dissolved in non-polar solvents such as hexane. The solutions are air-sensitive.

$[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10**. *Method* (a). A stirred solution of $[Co_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **5** (0.60 g, 0.67 mmol) in CH_2Cl_2 (100 cm^3) was treated with $[Co(\eta\text{-}C_5H_5)_2]$ (0.25 g, 1.33 mmol). After 5 min the solvent was removed *in vacuo* and the residue extracted with hexane (3 × 30 cm^3). The extract was filtered and heated under reflux for 12 h. After cooling to room temperature, the solution was filtered, evaporated to minimum volume and cooled to −10 °C for 18 h to give the product as maroon crystals. Concentration and cooling of the mother-liquors afforded more product, total yield 0.18 g (44%).

Method (b). A solution of $[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **8** (0.04 g, 0.06 mmol) in hexane (15 cm^3) was heated under reflux for 12 h. After cooling to room temperature, the solution was filtered and evaporated to dryness to give the product as a red powder, yield 0.03 g (76%).

The complex dissolves in non-polar solvents such as hexane to give air-sensitive solutions.

$[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **9**. Evaporation to a minimum volume of the mother-liquors from the preparation of $[Co_2(\sigma,\eta^3:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **8** or $[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10** and cooling to −78 °C for 18 h afforded the product as a red powder in yields of *ca.* 10%. The complex dissolves in non-polar solvents such as hexane to give air-sensitive solutions.

$[Co_2(\eta^2,\eta^3:\eta'^5\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2][PF_6]_2$ **13**. To a stirred solution of $[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10** (0.06 g, 0.10 mmol) in CH_2Cl_2 (20 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ (0.06 g, 0.20 mmol). After 5 min the orange solution was filtered and evaporated to low volume. Addition of diethyl ether (100 cm^3) gave an orange solid which was purified by dissolution in CH_2Cl_2, filtration, and precipitation with diethyl ether, yield 0.08 g (86%).

The complex is soluble in polar solvents such as CH_2Cl_2 and CH_3NO_2, giving solutions which slowly decompose in air.

$[Co(\eta^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)]$ **15**. A stirred mixture of $[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10** (0.15 g, 0.25 mmol) and $Me_3NO{\cdot}2H_2O$ (1.08 g, 9.71 mmol) in benzene (60 cm^3) was heated under reflux for 36 h. The solvent was then removed *in vacuo* and the residue extracted with hexane. The extract was chromatographed on an hexane–alumina column (10 × 3 cm), eluting with hexane. Evaporation of the solvent from the orange eluate gave the product as a brown solid, yield 0.05 g (52%).

The complex dissolves in non-polar solvents such as hexane to give air-sensitive solutions.

Crystal Structure Analysis of $[Co_2(\eta^4:\eta'^4\text{-}C_{16}H_{16})(\eta\text{-}C_5Me_5)_2]$ **10**.—*Crystal data.* $C_{36}H_{46}Co_2$, M = 596.6, monoclinic, space group $P2_1/c$, a = 15.247(4), b = 12.505(3), c = 16.073(4) Å, β = 100.60(2), U = 3012.2(12) $Å^3$, Z = 4, D_c = 1.36 g cm^{-3}, λ = 0.710 69 Å, μ = 11.2 cm^{-1}, $F(000)$ = 1264, T = 295 K.

Diffraction measurements were made with a Nicolet four-circle P3m diffractometer using graphite-monochromated X-ray radiation on a single crystal (approximate dimensions 0.55 × 0.13 × 0.25 mm) mounted in a thin-walled glass capillary under N_2. Cell dimensions were determined from the setting angle values of 15 centred reflections. A total of 6004 diffracted intensities (including checks) were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by ω–2θ scans of width $2.0° + \Delta_{\alpha_1\alpha_2}$. Three check reflections (8 0 0, 5 7 4, 0 0 8), remeasured after every 50 ordinary data, showed a 6% decay and *ca.* 1% variation over the period of data collection; an appropriate correction was therefore applied. Of the 5983 non-check intensity data collected, 5315 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences. Of these, 4091 with $I > 1.5\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 400 azimuthal scan data; maximum and minimum transmission coefficients were 0.530 and 0.489 respectively. Lorentz and polarisation corrections were applied. The structure was solved by heavy-atom (Patterson and difference Fourier) methods, and refined by blocked-cascade least squares against F. All non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms of the $C_{16}H_{16}$ ligand were refined without positional constraints, but with fixed isotropic displacement parameters. All other (methyl) hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å. Refinement of the 391 least-squares variables converged smoothly to residual indices $R = 0.053$, $R' = 0.061$, $S = 1.55$ ($R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; N_o = no. of observations N_v = no. of variables). Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$. Here $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0005$ was chosen to minimise the variation in S as a function of F_o. Final difference electron density maps showed no features outside the range +0.4 to −0.4 e Å^{-3}. Table 4 gives the positional parameters for the non-hydrogen atoms.

All calculations were made with programs of the SHELXTL[27] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 28.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for Research Studentships (to B. J. D. and M. G.).

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Received 30*th July* 1990; *Paper* 0/03460F