Preparation of a Bis(cyclopentadienyl)acetylene-framed Heterobimetallic Complex and its Reaction with Dicobalt Octacarbonyl †

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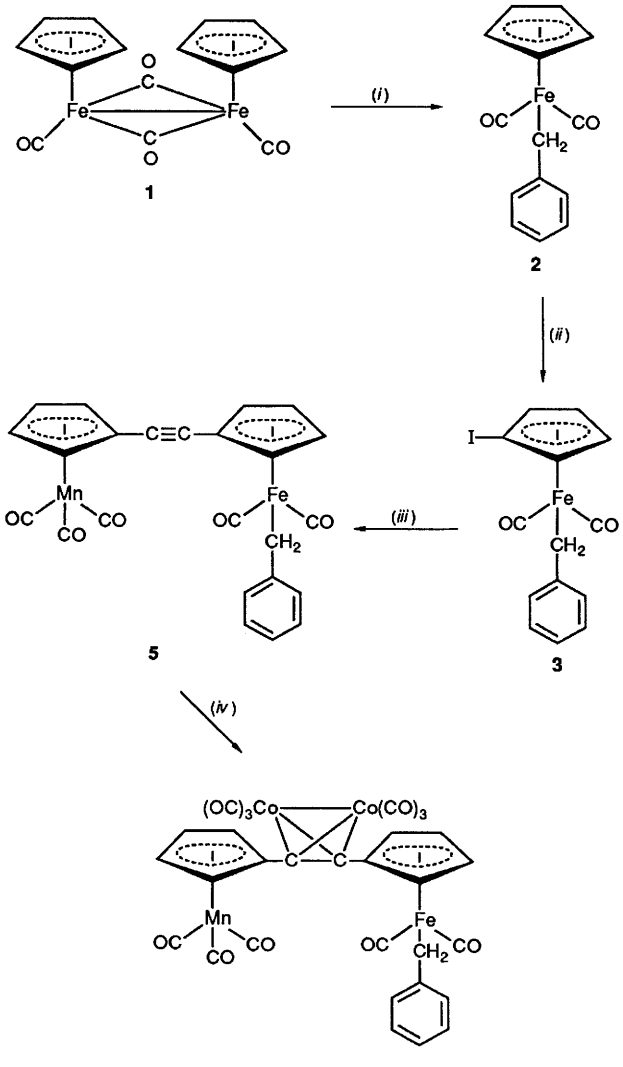
The bis(cyclopentadienyl)acetylene-framed heterobimetallic complex $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)\}Fe(CO)_2(CH_2Ph)]$ has been prepared by two consecutive palladium-catalysed coupling reactions from the corresponding iodocyclopentadienyl monometallic complexes $[Mn(\eta^5\text{-}C_5H_4I)(CO)_3]$ and $[Fe(\eta^5\text{-}C_5H_4I)(CO)_2(CH_2Ph)]$. Reaction of the heterobimetallic compound with $[Co_2(CO)_8]$ affords quantitatively the dicobalt adduct $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)C(OC)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)\}Fe(CO)_2(CH_2Ph)]$. The X-ray structure of this complex shows a closer proximity between the two metal centres than some previously reported analogues.

In the past few years, by means of the palladium-catalysed coupling reaction, we were able to prepare a number of bis(cyclopentadienyl) framed polymetallic complexes.[1,2] Such species are interesting for their potential use in catalysis and in the study of multicentre co-operative interactions between different metal centres in chemical transformations of small molecules.[3] The generality of the synthetic procedure that we discovered has allowed us to couple quite a large variety of cyclopentadienyl metal complexes in such a way that many different combinations of metals can be introduced in the same molecular unit. This characteristic allows variation of the synthetic procedure in order to 'tune' the final product toward the properties desired. We report here the preparation of a heterobimetallic complex of Mn^I and Fe^{II} where the two metal centres are joined by a bis(cyclopentadienyl)acetylene ligand. The acetylene bridge between the two cyclopentadienyl rings allowed a further elaboration of the complex by reaction with dicobalt octacarbonyl, to form the typical dicobalt 'butterfly' adduct.

Results and Discussion

The assembly of the heterobimetallic complex $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)\}Fe(CO)_2(CH_2Ph)]$ **5** was accomplished by the well known palladium-catalysed route[4,5] between the two appropriately functionalized partners as illustrated in Scheme 1.The complex $[Fe(\eta^5\text{-}C_5H_4I)(CO)_2(CH_2Ph)]$ **3** was obtained by treatment of the cyclopentadienyliron dicarbonyl dimer $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ **1** with NaK alloy, and subsequent quenching of the resulting monomeric anion[6] with benzyl bromide, to give $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2Ph)]$ **2** in 58% yield. Subsequent treatment of this complex with $LiBu^s$ and iodine in tetrahydrofuran (thf) at −78 °C afforded **3** in 53% yield. Following a previously described procedure,[2] the coupling partner $[Mn\{\eta^5\text{-}C_5H_4C{\equiv}C(SnMe_3)\}(CO)_3]$ **4** was prepared by reaction of Me_3SnNEt_2 and $[Mn(\eta^5\text{-}C_5H_4C{\equiv}CH)(CO)_3]$, which in turn was obtained by the palladium-catalysed coupling reaction of $[Mn(\eta^5\text{-}C_5H_4I)(CO)_3]$[1] and $Bu_3SnC{\equiv}CH$. Coupling of **4** and **3** was accomplished in dimethylformamide (dmf)



Scheme 1 (*i*) (*a*) Na/K alloy, (*b*) $PhCH_2Br$; (*ii*) (*a*) $LiBu^s$, (*b*) I_2; (*iii*) compound **4**, 5% $[PdCl_2(MeCN)_2]$; (*iv*) $[Co_2(CO)_8]$

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

in the presence of 5 mol% of $[PdCl_2(MeCN)_2]$ at room temperature. After work-up and separation by column chromatography, the coupled product **5** was isolated in 74% yield, as a yellow oil that solidified on standing. The acetylenic moiety between the two rings C_5H_4 of the heterobimetallic complex **5** was then used as a site of attack for further structural elaboration. Reaction of **5** with $[Co_2(CO)_8]$ was straightforward.[1] The two reactants, stirred in benzene, underwent complete transformation in 2 h. The pure product was isolated in a nearly quantitative yield by column chromatography. Recrystallization from thf–pentane by vapour diffusion at 5 °C afforded dark red crystals suitable for X-ray determination.

A single-crystal X-ray diffraction analysis of compound **6** revealed the molecular structure shown in Fig. 1. The most interesting structural features of this complex can be better discussed by comparison with those of the analogous compounds $[Me(OC)_3W\{(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)\}Mn(CO)_2(PPh_3)]$ **7** and $[I(OC)_2Fe\{(\eta^5\text{-}C_5H_4)C(OC)_3Co{-}Co(CO)_3C(\eta^5\text{-}C_5H_4)\}Fe(CO)_2I]$ **8** previously published[1,2] (Fig. 2).

In building these structures, our effort has been directed to having the metal centres in such a geometrical array that their ancillary ligands would be exposed to the simultaneous influence of the different metals. In this situation the synergic effect of the metals on the ligands could lead to new reaction pathways otherwise impossible.

The structure of the simple heterobimetallic complex **7**, where the angle formed by the lines connecting the metals with the centroids of the C_5H_4 rings is 163.3°, shows an almost perfect 'transoid' configuration between the two metal centres with respect to the ligand plane. The linear acetylenic bond places the centroids of the two rings at a distance of 6.447 Å, and the two metals at 7.597 Å which is too large for any interaction between them. The dihedral angle observed between the mean C_5H_4 ring planes is 15.6°. This small distortion with respect to the perfect 'flat' conformation of a similar compound[7] can be related to the linearity of the connection between the rings, which avoids any steric hindrance between the triphenylphosphine ligand and the opposite cyclopentadienyl group by twisting the two C_5H_4 planes.

By reaction of the alkyne bridge of a compound like **7** with $[Co_2(CO)_8]$ the general array of the complex is heavily distorted by the formation of bonds between the cobalt atoms and the carbon atoms of the bridge which modify their configuration from sp to sp^3. The extent of this distortion and the reciprocal orientation of the C_5H_4 rings are probably dependent both on the kind of metals and on the type of the different groups connected to the metals. The aliphatic bond distance [C(1)–C(16) 1.338(10) Å] of compound **6** is comparable with that found in **8** [C(6)–C(7) 1.349(5) Å], while the distance between the centroids of the two C_5H_4 rings in **6** (5.632 Å) differs significantly from those reported for **8** (5.693 Å) (both significantly shorter when compared with that of **7**). This fact is probably due to the difference in the reciprocal orientation of rings which form a dihedral angle of 39.5° in compound **6** and of 31.7° in **8**. Even though the two η^5-bonded metals are still twisted in opposite directions, the degree of torsion between the two C_5H_4 rings is more severe and the two η^5-complexed metals are closer than in **7**. Moreover, there are noticeable differences in the distances between the heavy atoms and the centroids of the opposite C_5H_4 rings: the Fe and Mn atoms are 5.492 and 5.892 Å from the centroids of the C(17)···C(21) and C(2)···C(6) rings in our derivative, respectively, while the distances between the iron atoms and the centroids of the opposite C_5H_4 rings are 5.756 and 5.828 Å in **8**. In addition, the metal centres in **6** and **8** are very close to the cobalt atoms, so that an interaction between them and cobalt is possible. A detailed analysis of these complexes reveals that the Mn–Fe and Fe–Fe distances in **6** and **8** are 6.152 and 6.287 Å, respectively, and while in **8** the Co(1) and Co(2) atoms are at distances of 5.152, 4.349 and 4.489, 5.111 Å from Fe(1) and Fe(2), respectively, in compound **6** the cobalt atoms show distances of 4.612, 5.146 and 5.134, 4.340 Å from Fe and Mn atoms, respectively. These small but significant differences in the spatial arrangement of the two compounds, depending on the different kinds of heavy atoms and on their different substituents, do not give rise to a markedly different 'transoid' configuration: in fact the angles between the lines connecting the metals with the centroids of their C_5H_4 rings are 145.2° in both compounds. As previously observed in analogous derivatives, the C–Fe–C and the C–Mn–C angles average 89.5(2) and 91.3(2)°, respectively, and the dicobalt-substituted fragment is practically perpendicular (88.0°) to the C(1)–C(16) bond. Normal van der Waals interactions connect the molecules in the crystal.

Table 1 Crystal data and X-ray experimental information for compound **6**

Formula	$C_{30}H_{15}Co_2FeMnO_{11}$
M	780.09
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	16.020(2)
b/Å	11.863(2)
c/Å	15.893(2)
β/°	102.04(2)
U/Å^3	2953.95
T/°C	22–24
F(000)	1552
D_c/g cm^{-3}	1.75
μ/cm^{-1}	169.4
Z	4
Diffractometer	Siemens AED
Crystal dimensions/mm	0.15 × 0.27 × 0.39
Radiation	Cu-Kα (λ = 1.5418 Å)
θ range/°	3–70
Collected indices	$\pm h, +k, +l$
Reflections:	
total independent	5611
observed [$I > \sigma(I)$]	3298
Final R	0.074
Final R' *	0.067

* Weighting scheme $w = k/(\sigma^2F + gF^2)$, where $k = 0.2884$ and $g = 0.006\,78$.

Experimental

X-Ray Analysis.—Crystal data together with details of the X-ray analysis are in Table 1. Cell parameters were obtained by least-squares treatment of angular $(\theta, \chi, \varphi)_{hkl}$ values of 30 reflections automatically well centred on the diffractometer. One check reflection, monitored every 50, showed decomposition of the specimen by about 10% during the data collection. The intensities were corrected for this decay and for Lorentz and polarization effects. The structure was solved by automated Patterson methods with the program XFPS 90.[8] Isotropic full-matrix refinement of all heavy atoms, carried out with SHELX 76,[9] gave an agreement value R of 0.074. The absorption correction was performed following Walker and Stuart[10] with the program ABSORB.[11] The maximum and minimum values of the absorption coefficients in the polar angles φ and μ are 1.26 and 0.38, respectively. All the H atoms were found in a ΔF map computed after some block-matrix anisotropic cycles. All the calculations were performed on a IBM PS2/80 personal computer with the CRYSRULER package.[12] The final atomic coordinates are in Table 2, while Tables 3 and 4 list selected bond distances and angles, respectively.

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

General Procedure.—All reactions were performed under

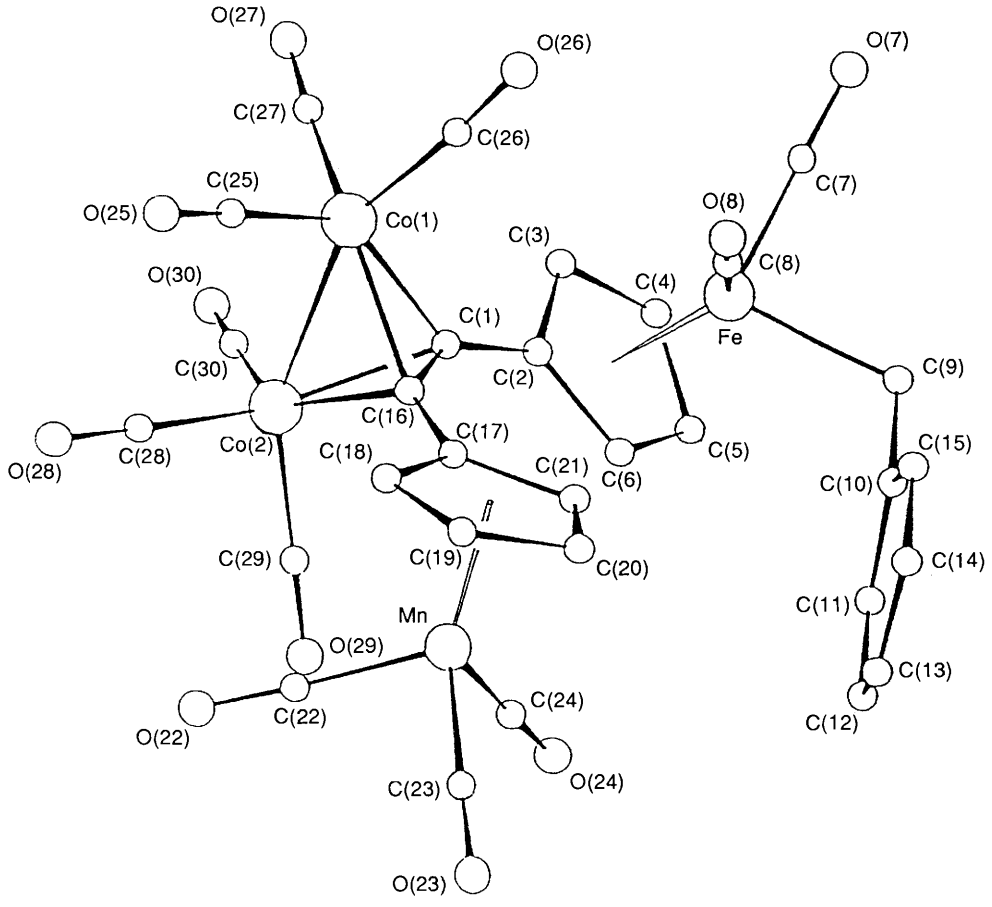


Fig. 1 Projection of the molecule **6** with arbitrary numbering scheme. Hydrogen atoms were omitted for clarity

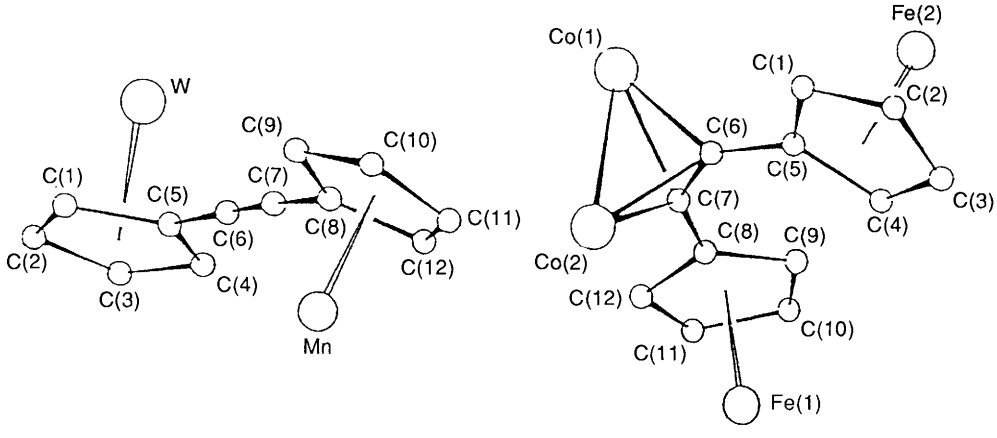


Fig. 2 Drawings of the bis(cyclopentadienyl)-bridged framework and the metal atoms of compounds **7** and **8**. Hydrogen atoms and ancillary ligands have been omitted for clarity

argon by use of standard Schlenk techniques. Tetrahydrofuran and benzene were distilled over sodium–benzophenone; dmf was distilled under vacuum from CaH_2. The compounds $[PdCl_2(MeCN)_2]$[13] and $[Mn\{\eta^5\text{-}C_5H_4C{\equiv}C(SnMe_3)\}(CO)_3]$[2] were prepared as previously described, LiBu^s and $[Co_2(CO)_8]$ were purchased from Aldrich and used as received. Proton NMR spectra were recorded on a Bruker WP80 instrument operating at 80 MHz, ^{13}C NMR on a Varian XL300 instrument operating at 75 MHz. The chemical shifts are reported in ppm *vs.* $SiMe_4$, by assigning the ^1H impurity in the solvent ($CDCl_3$) at δ 7.24. The ^{13}C spectral chemical shifts are relative to the ^{13}C triplet ($CDCl_3$) at δ 77.00. Infrared (IR) spectra were recorded on a Nicolet FT 510 instrument in the solvent-subtraction mode. Melting points were determined in an open capillary on a Buchi 510 apparatus. Elemental analyses were performed by the Servizio Microanalisi of the Area della Ricerca di Roma (Consiglio Nazionale delle Ricerche, Monterotondo).

$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2Ph)]$ **2**.—This compound was prepared by treating $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ **1** (2.82 g, 7.96 mmol) with $NaK_{2.8}$ alloy (1.0 cm^3) in thf (60 cm^3) to form the corresponding anion $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ as described in the literature.[5] Benzyl bromide (1.362 g, 7.96 mmol) was then added by syringe and stirring continued for 6 h at room temperature. Removal of the solvent *in vacuo* gave a crude oily residue which was mixed with Celite (20 g) and transferred on to a chromatographic column packed with silica gel. An orange band was collected by elution with hexane. Removal of the solvent left the

Table 2 Atomic fractional coordinates ($\times 10^4$) for compound **6**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/a*	*Z/c*
Co(1)	3029(1)	497(1)	4376(1)	C(9)	4313(6)	−4305(8)	3215(7)
Co(2)	1764(1)	324(1)	3212(1)	C(10)	3609(6)	−4890(7)	3494(6)
Fe	4180(1)	−2528(1)	3192(1)	C(11)	2877(8)	−5221(9)	2902(9)
Mn	752(1)	−2553(1)	4359(1)	C(12)	2211(9)	−5749(10)	3190(13)
O(7)	6013(4)	−2324(8)	3450(5)	C(13)	2284(10)	−5939(9)	4101(14)
O(8)	4253(4)	−2622(5)	5003(4)	C(14)	3006(9)	−5685(9)	4632(10)
O(22)	−498(4)	−794(5)	3710(4)	C(15)	3658(7)	−5158(8)	4350(8)
O(23)	−623(3)	−4042(5)	4665(4)	C(16)	2244(4)	−805(5)	4079(4)
O(24)	723(4)	−3569(5)	2685(4)	C(17)	1933(4)	−1615(5)	4624(4)
O(25)	2173(4)	1713(6)	5553(4)	C(18)	1435(4)	−1370(6)	5242(5)
O(26)	4411(4)	−319(5)	5718(4)	C(19)	1330(4)	−2344(7)	5683(5)
O(27)	4025(4)	2108(5)	3565(4)	C(20)	1726(4)	−3254(6)	5334(5)
O(28)	597(4)	1680(6)	3979(5)	C(21)	2112(4)	−2808(5)	4685(5)
O(29)	498(4)	−975(5)	2025(4)	C(22)	−21(4)	−1505(6)	3944(5)
O(30)	2340(5)	1668(8)	1905(5)	C(23)	−93(4)	−3449(6)	4544(5)
C(1)	2760(4)	−712(5)	3520(4)	C(24)	724(4)	−3177(7)	3346(5)
C(2)	3155(4)	−1327(6)	2924(4)	C(25)	2512(5)	1281(7)	5095(6)
C(3)	3843(5)	−953(7)	2567(5)	C(26)	3870(5)	−40(6)	5172(5)
C(4)	3978(6)	−1786(8)	1960(5)	C(27)	3634(4)	1517(6)	3890(5)
C(5)	3381(6)	−2672(8)	1957(6)	C(28)	1036(5)	1168(7)	3671(6)
C(6)	2882(4)	−2408(6)	2365(5)	C(29)	992(5)	−483(6)	2488(5)
C(7)	5290(5)	−2415(8)	3355(6)	C(30)	2113(6)	1176(7)	2414(7)
C(8)	4212(4)	−2587(6)	4270(5)				

Table 3 Selected bond distances (Å) for compound **6**

Co(1)–Co(2)	2.451(2)	Fe–C(7)	1.748(8)
Co(1)–C(1)	1.962(6)	Fe–C(8)	1.705(8)
Co(1)–C(16)	1.985(6)	Fe–C(9)	2.118(10)
Co(1)–C(25)	1.803(10)	Mn–C(17)	2.159(6)
Co(1)–C(26)	1.764(7)	Mn–C(18)	2.120(7)
Co(1)–C(27)	1.820(8)	Mn–C(19)	2.129(8)
Co(2)–C(1)	1.992(6)	Mn–C(20)	2.126(7)
Co(2)–C(16)	1.960(6)	Mn–C(21)	2.153(6)
Co(2)–C(28)	1.803(9)	Mn–C(22)	1.781(7)
Co(2)–C(29)	1.782(7)	Mn–C(23)	1.793(7)
Co(2)–C(30)	1.800(11)	Mn–C(24)	1.764(8)
Fe–C(2)	2.148(7)	C(1)–C(2)	1.442(10)
Fe–C(3)	2.132(8)	C(1)–C(16)	1.338(10)
Fe–C(4)	2.109(8)	C(9)–C(10)	1.469(14)
Fe–C(5)	2.115(9)	C(16)–C(17)	1.450(9)
Fe–C(6)	2.115(6)		

Table 4 Selected bond angles (°) for compound **6** [BAR1 and BAR2 refer to the barycentre of the C(2)–C(6) and C(17)–C(21) rings, respectively]

C(26)–Co(1)–C(27)	98.6(3)	C(23)–Mn–C(24)	91.4(3)
C(25)–Co(1)–C(27)	106.4(3)	C(22)–Mn–C(24)	94.1(3)
C(25)–Co(1)–C(26)	96.6(3)	C(22)–Mn–C(23)	89.1(3)
C(16)–Co(1)–C(27)	141.6(3)	BAR2–Mn–C(22)	124.0(4)
C(16)–Co(1)–C(26)	103.9(3)	BAR2–Mn–C(23)	125.1(4)
C(16)–Co(1)–C(25)	101.5(3)	BAR2–Mn–C(24)	123.4(3)
C(1)–Co(1)–C(27)	104.5(3)	Fe–C(9)–C(10)	113.2(6)
C(1)–Co(1)–C(26)	104.9(3)	Co(1)–C(1)–Co(2)	76.6(2)
C(1)–Co(1)–C(25)	138.9(3)	Co(2)–C(1)–C(16)	68.9(3)
C(1)–Co(1)–C(16)	39.6(2)	Co(2)–C(1)–C(2)	126.1(4)
Co(2)–Co(1)–C(27)	99.5(2)	Co(1)–C(1)–C(16)	71.1(3)
Co(2)–Co(1)–C(26)	154.0(2)	Co(1)–C(1)–C(2)	139.7(4)
Co(2)–Co(1)–C(25)	96.0(2)	C(2)–C(1)–C(16)	144.2(6)
Co(2)–Co(1)–C(16)	51.1(1)	C(1)–C(2)–C(6)	125.1(5)
Co(2)–Co(1)–C(1)	52.3(1)	C(1)–C(2)–C(3)	126.2(6)
Co(1)–Co(2)–C(30)	98.9(3)	C(9)–C(10)–C(15)	121.0(9)
Co(1)–Co(2)–C(29)	152.3(2)	C(9)–C(10)–C(11)	121.2(9)
Co(1)–Co(2)–C(28)	98.7(3)	Co(2)–C(16)–C(1)	71.5(3)
Co(1)–Co(2)–C(16)	52.1(1)	Co(1)–C(16)–C(1)	69.2(3)
Co(1)–Co(2)–C(1)	51.1(1)	Co(1)–C(16)–Co(2)	76.8(2)
C(29)–Co(2)–C(30)	97.0(4)	C(1)–C(16)–C(17)	142.0(6)
C(28)–Co(2)–C(30)	107.2(3)	Co(2)–C(16)–C(17)	137.7(4)
C(28)–Co(2)–C(29)	98.0(3)	Co(1)–C(16)–C(17)	130.8(4)
C(16)–Co(2)–C(30)	138.2(3)	C(16)–C(17)–C(21)	127.0(5)
C(16)–Co(2)–C(29)	101.8(3)	C(16)–C(17)–C(18)	126.2(5)
C(16)–Co(2)–C(28)	106.7(3)	Fe–BAR1–C(2)	91.8(6)
C(1)–Co(2)–C(30)	99.7(3)	Fe–BAR1–C(3)	90.3(6)
C(1)–Co(2)–C(29)	103.9(3)	Fe–BAR1–C(4)	89.4(7)
C(1)–Co(2)–C(28)	142.7(3)	Fe–BAR1–C(5)	89.5(6)
C(1)–Co(2)–C(16)	39.6(2)	Fe–BAR1–C(6)	89.5(6)
C(8)–Fe–C(9)	87.7(3)	Mn–BAR2–C(17)	90.9(5)
C(7)–Fe–C(9)	88.8(4)	Mn–BAR2–C(18)	89.3(5)
C(7)–Fe–C(8)	92.2(4)	Mn–BAR2–C(19)	90.0(5)
BAR1–Fe–C(7)	125.5(4)	Mn–BAR2–C(20)	89.2(5)
BAR1–Fe–C(8)	128.5(4)	Mn–BAR2–C(21)	90.7(5)
BAR1–Fe–C(9)	122.4(4)		

pure product as a yellow oil (1.22 g, 58%). IR (CCl_4): 2013.5vs and 1963.3vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.12–6.93 (m, 5 H, Ph), 4.62 (s, 5 H, C_5H_4) and 2.67 (s, 2 H, CH_2); ^{13}C, δ 216.71 (CO), 152.52, 131.03, 128.91, 116.00 (Ph), 85.87 (C_5H_4) and 4.08 (CH_2) (Found: C, 62.30; H, 4.10. Calc. for $C_{14}H_{12}FeO_2$: C, 62.70; H, 4.50%).

$[Fe(\eta^5\text{-}C_5H_4I)(CO)_2(CH_2Ph)]$ **3**.—The compound LiBu^s (3.5 cm^3, 4.55 mmol, 1.3 mol dm^{-3} solution in hexane) was added to a stirred solution of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2Ph)]$ **2** (1.22 g, 4.55 mmol) in thf (40 cm^3) cooled at −78 °C. After 15 min of stirring at low temperature, iodine (1.14 g, 4.55 mmol) dissolved in thf (50 cm^3) was added by cannula, and the cold-bath was removed. The stirring was continued for 30 min, then removal of the solvent *in vacuo* left the crude residue. Celite (20 g) and CH_2Cl_2 (50 cm^3) were added, the solvent was removed and the coated product was chromatographed on silica using hexane as eluent; 0.95 g (53%) of product was isolated as a yellow oil, m.p. 67–68 °C. IR (CCl_4): 2014.2vs and 1963.8vs cm^{-1}. NMR($CDCl_3$): ^1H, δ 7.24–6.95 (m, 5 H, Ph), 4.82 (t, 2 H, *J* 2.12, C_5H_4), 4.56 (t, 2 H, *J* 2.12 Hz, C_5H_4) and 2.78 (s, 2 H, CH_2); ^{13}C, δ 216.24 (CO), 152.18, 128.18, 127.56, 123.45 (Ph), 94.75, 85.06, 47.17 (C_5H_4) and 9.69 (CH_2) (Found: C, 42.65; H, 2.80. Calc. for $C_{14}H_{11}FeIO_2$: C, 42.65; H, 2.80%).

$[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)\}Fe(CO)_2(CH_2Ph)]$

5.—Under argon atmosphere, a Schlenk flask (100 cm^3) was charged with $[Mn\{\eta^5\text{-}C_5H_4C{\equiv}C(SnMe_3)\}(CO)_3]$ **4** (0.53 g, 1.35 mmol), **3** (0.525 g, 1.35 mmol) and dmf (50 cm^3). While stirring, $[PdCl_2(MeCN)_2]$ (0.017 g, 0.06 mmol) dissolved in dmf (5 cm^3) was added by a syringe. Stirring was continued at room temperature for 8h, then the mixture was diluted with Et_2O (200

cm^3) and transferred to a separatory funnel (500 cm^3). The solution was washed with water (3 × 50 cm^3) and the aqueous phase was back-extracted with diethyl ether (2 × 50 cm^3). The combined ether extracts were dried over magnesium sulphate, filtered then Celite (20 g) was added and evaporated to dryness *in vacuo*. The residue, added to a chromatography column packed with silica and eluted with a 10% mixture of ethyl acetate in hexanes, gave after evaporation of the solvent under vacuum 0.49 g, (74%) of the product as an orange oil, m.p. 99–100 °C. IR (CCl_4): 2029.7vs, 2012.9vs, 1961.8 (sh) and 1950.7vs cm^{-1}. NMR ($CDCl_3$): ^1H, 7.20–6.93 (m, 5 H, Ph), 5.03 (t, 2 H, *J* 2.14, MnC_5H_4), 4.86 (t, 2 H, *J* 2.22, FeC_5H_4), 4.70 (t, 2 H, *J* 2.14, MnC_5H_4), 4.61 (t, 2 H, *J* 2.22, FeC_5H_4), 2.84 (s, 2 H, CH_2); ^{13}C, δ 223.92 (MnCO), 215.74 (FeCO), 152.29, 128.10, 127.51, 123.37 (Ph), 90.55, 88.10, 86.65, 84.13, 82.32, 82.04, 81.81, 81.27 (ligand frame) and 8.58 (CH_2) (Found: C, 58.55; H, 3.00. Calc. for $C_{24}H_{15}FeMnO_5$: C, 58.35; H, 3.05%).

$[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)C(OC)_3Co\text{–}Co(CO)_3C(\eta^5\text{-}C_5H_4)\}$

$Fe(CO)_2(CH_2Ph)]$ **6**.—Compound **5** (0.40 g, 0.80 mmol) was dissolved in benzene (50 cm^3) and stirred at room temperature. The compound $[Co_2(CO)_8]$ (0.30 g, 0.89 mmol) was added and stirring continued for 2 h. Celite (20 g) was added to the crude mixture and the solvent was removed *in vacuo*. The residue was then chromatographed over silica using a mixture of hexane–ethyl acetate (8:2) as eluent. Pure product was recovered (0.61 g, 97%) as a dark red solid. Recrystallization by vapour diffusion at −20 °C from thf–pentane afforded X-ray-quality black crystals, m.p. 133–134 °C, IR (CCl_4): 2094.2m, 2061.5vs, 2032.4vs, 2024.5s, 2005.8m and 1950.5vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.17–7.00 (m, 5 H, Ph), 5.26 (t, 2 H, *J* 2.17, MnC_5H_4), 5.14 (t, 2 H, *J* 2.15, FeC_5H_4), 4.75 (t, 2 H, *J* 2.17, MnC_5H_4), 4.57 (t, 2 H, *J* 2.15, FeC_5H_4), 2.80 (s, 2 H, CH_2); ^{13}C, δ 224.31 (MnCO), 216.38 (FeCO), 198.15 (CoCO), 152.15, 128.24, 127.38, 123.46 (Ph), 98.93, 98.46, 88.36, 88.03, 87.90, 84.25. 81.08 (ligand frame) and 6.23 (CH_2) (Found: C, 45.95; H, 1.90. Calc. for $C_{30}H_{15}Co_2FeMnO_{11}$: C, 46.20; H, 1.95%).

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