Crystal Structures of a Bis(cyclopentadienyl)(*Z*)-enyne Framed Manganese(I)–Rhenium(I) Complex and its $[Co_2(CO)_8]$ Adduct†

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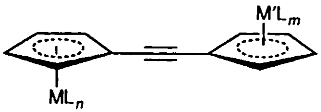
The X-ray structural determination of the manganese(I)–rhenium(I) complex $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)(Z)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)\}Re(CO)_3]$ **1** has been carried out. The structural data show that the (*Z*)-enyne linkage between the two cyclopentadienyl rings, despite the conjugation that would keep the ligand framework coplanar, allows twisting of the two cyclopentadienylmetal units. Because of this characteristic the Mn···Re interatomic distance (6.1 Å) is much shorter than in similar bis(cyclopentadienyl)-linked heterobimetallic complexes. Reaction of **1** with $[Co_2(CO)_8]$ affords quantitatively the corresponding dicobalt tetragonal pyramidal adduct $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)(Z)CH{=}CHC\text{–}(OC)_3Co\text{–}Co(CO)_3\text{–}C\text{–}(\eta^5\text{-}C_5H_4)\}Re(CO)_3]$ **2** the X-ray structure of which has been determined. The presence of the dicobalt unit on the triple bond heavily affects the carbon chain connecting the two cyclopentadienyl rings, and the metal centres are at a larger distance than in **1**. Crystal data: **1**, triclinic, space group $P\bar{1}$, $a = 6.546(1)$, $b = 11.066(2)$, $c = 13.451(3)$ Å, $\alpha = 96.06(2)$, $\beta = 100.46(2)$, $\gamma = 96.31(1)°$, $R(F) = 0.0466$, $R'(F) = 0.0542$ for 2710 observed reflections with $F > 4.0\sigma(F)$; **2**, triclinic, space group $P\bar{1}$, $a = 9.825(3)$, $b = 11.853(4)$, $c = 13.662(3)$ Å, $\alpha = 109.41(2)$, $\beta = 104.36(2)$, $\gamma = 99.16(2)°$, $Z = 2$, $R(F) = 0.0325$, $R'(F) = 0.0352$ for 5913 observed reflections with $F > 4.0\sigma(F)$.

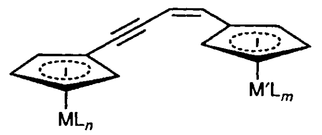
In recent years the preparation of new heteropolymetallic complexes has been a subject of widespread interest, because of the possible enhancement of catalytic activity with respect to the corresponding individual monometallic components.[1] Our interest in this area has been focused on the preparation of heterobimetallic species having the two metal units coordinated by cyclopentadienyl groups, linked through a suitable carbon chain. Our preference for cyclopentadienyl complexes arises from the well known binding ability of this ligand toward transition metals and consequently the large variety of metals that can be combined to form the bimetallic pair.

At first, by means of a palladium-catalysed coupling reaction, we formed a variety of heterobimetallic complexes in which two cyclopentadienyl metal complexes were linked with an acetylenic bridge.[2] The X-ray structural determination of such complexes shows that, at least in the solid state, the two metal centres lie in a 'transoid' configuration with respect to the bis(cyclopentadienyl) ligand plane (structure I). This conformation, along with the large interatomic distance (7.6 Å), makes any interaction between the two metal centres unfavourable, although in solution free rotation of the two C_5H_4 rings could bring the metal centres on the same side of the ligand plane. Subsequently, by modification of the above-mentioned synthetic route, the two C_5H_4 rings were connected by a (*Z*)-enyne bridge[3] (structure II).

The choice of binding the two cyclopentadienyl units by a (*Z*)-enyne linkage came from the expectation that the constraint imposed by the (*Z*) geometry of the double bond upon the general ligand framework would bring the two metal units much closer together than in corresponding compounds having only an acetylenic spacer between the rings. Moreover, we thought that, if the coplanarity imposed by the conjugation between the two C_5H_4 rings through the enyne linkage could be broken, then it would be possible for the two metal centres to be very close together.



I



II

Experimental

Standard techniques, with Schlenk-type equipment for the manipulation of air-sensitive compounds under prepurified argon or vacuum, were employed. The NMR spectra were run on Bruker WP80 and Varian XL300 spectrometers and IR spectra 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). Benzene was dried and deoxygenated by sodium/potassium–benzophenone prior to use.

The compound $[(OC)_3Mn\{(\eta^5\text{-}C_5H_4)(Z)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)\}Re(CO)_3]$ **1** was prepared by the procedure described

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

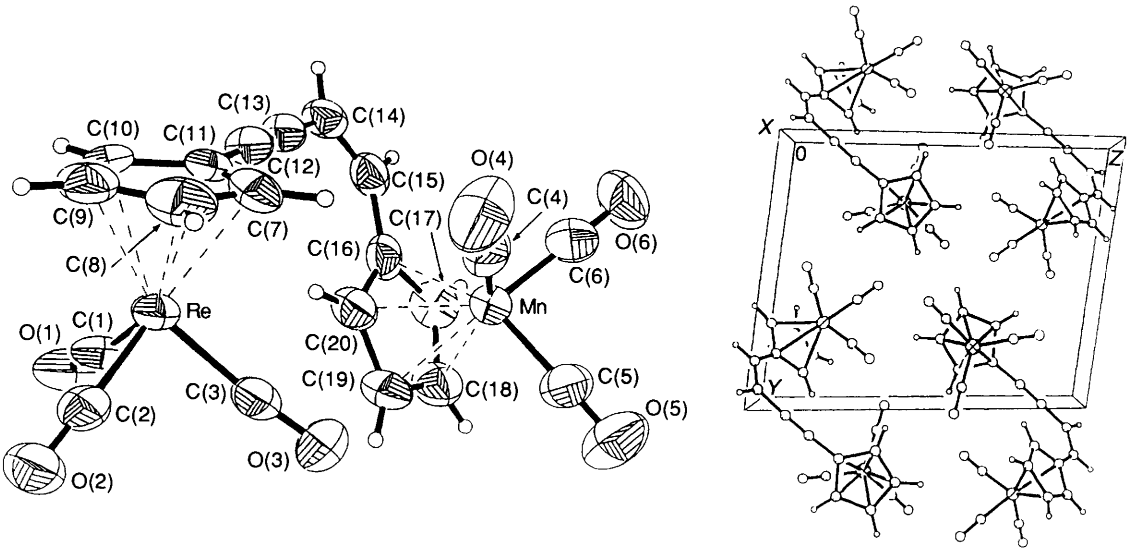


Fig. 1 An ORTEP[4b] drawing and the crystallographic unit cell of complex **1**. Thermal ellipsoids are drawn at the 50% probability level and, for the sake of clarity, the hydrogen atoms are artificially small

Table 1 Summary of crystallographic data *

(*a*) Crystal parameters		
Formula	$C_{20}H_{10}MnO_6Re$	$C_{26}H_{10}Co_2MnO_{12}Re$
M	587.4	873.3
Colour, habit	Orange, parallelopipeds	Dark violet, parallelopipeds
Crystal size/mm	0.15 × 0.15 × 0.25	0.2 × 0.2 × 0.9
a/Å	6.546(1)	9.825(3)
b/Å	11.066(2)	11.853(4)
c/Å	13.451(3)	13.662(3)
α/°	96.06(2)	109.41(2)
β/°	100.46(2)	104.36(2)
γ/°	96.31(1)	99.16(2)
U/Å^3	941.0((1.2)	1401.7(7)
D_c/g cm^{-3}	2.073	2.069
μ/mm^{-1}	7.19	6.01
F(000)	556	832
(*b*) Data collection		
Scan limits θ/°	3–50	5–60
Scan speed/° min^{-1}	variable; 3.50 to 14.65 in ω	variable; 4.51 to 14.65 in ω
Scan range	0.65° plus Kα separation	0.60° plus Kα separation
Index ranges	$0 < h < 7, -13 < k < 13, -15 < l < 15$	$0 < h < 13, -16 < k < 16, -19 < l < 18$
No. independent reflections	3324	8229
No. observable reflections [$F > 4.0\sigma(F)$]	2710	5913
(*c*) Solution and refinement		
Hydrogen atoms (riding model)	$U = 0.06$ Å^2	$U = 0.067$ Å^2
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0010F^2$	$\sigma^2(F) + 0.0004F^2$
No. of parameters refined	255	380
Final R, R' (observed data)	0.0466, 0.0542	0.0325, 0.0352
(All data)	0.0604, 0.0591	0.0550, 0.0416
Goodness of fit	1.35	1.11
Largest and mean Δ/σ^2	0.041, 0.005	0.018, 0.014
Data to parameter ratio	10.6:1	15.6:1
Largest difference peak/e Å^{-3}	2.06 (0.9 Å from Re)	1.73 (0.8 Å from Re)
Largest difference hole/e Å^{-3}	−2.39	−0.95

* Details in common: crystal system, triclinic; space group $P\bar{1}$; $Z = 2$; 294 K; Siemens R3m/V diffractometer; Mo-Kα radiation ($\lambda = 0.710\,73$ Å); highly oriented graphite-crystal monochromator; ω–2θ scan method; two standard reflections per 100; Siemens SHELXTL PLUS; [4a] heavy-atom method; full-matrix least-squares refinement; quantity minimized $\Sigma w(|F_o| - |F_c])^2$.

previously.[2] Although we described the compound as an oil, after several attempts it was crystallized as yellow needles by slow diffusion of pentane into a concentrated solution of tetrahydrofuran (thf) at 4 °C, m.p. 92–93 °C.

Formation of Compound **2** *by Reaction of* **1** *and* [$Co_2(CO)_8$].—Compound **1** (0.092 g, 0.156 mmol) and [$Co_2(CO)_8$] (0.058 g, 0.172 mmol) were mixed in benzene (20 cm^3) and stirred at room temperature for 1 h. The solvent was removed and the flask connected to a high-vacuum line to remove excess of [$Co_2(CO)_8$], yielding 0.132 g, (100%) of product as a black solid, which was recrystallized at room temperature in the dark by vapour diffusion from thf–pentane, m.p. 139–140 °C (Found: C, 35.40; H, 1.10. Calc. for $C_{26}H_{10}Co_2MnO_{12}Re$: C, 35.75; H, 1.15%). IR (CCl_4): 2095.4s, 2061.7vs, 2034.1vs, 2025.7vs and 1942.8vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 6.65 (d, 1 H, J = 11.1, HC=), 6.46 (d, 1 H, J = 11.1, HC=), 5.71 (t, 2 H, J = 2.2, ReC_5H_4), 5.30 (t, 2 H, J = 2.2, ReC_5H_4), 4.91 (t, 2 H, J = 2.0, MnC_5H_4) and 4.71 (t, 2 H, J = 2.0 Hz, MnC_5H_4); ^{13}C, δ 224.48 (MnCO), 198.56 (CoCO), 193.35 (ReCO), 128.76 (=CH), 128.03 (=CH), 102.44 (C≡), 98.33 (C≡), 88.56, 87.14, 84.58 (ReC_5H_4), 83.81, 83.06 and 82.08 (MnC_5H_4).

Crystallography.—Crystals of compound **1**, while of adequate size, were of poor habit, being split or broken tubes or shards. On the contrary, crystals of **2** were of excellent quality. Details of crystal data, measurements of intensity and data processing are summarized in Table 1. An empirical absorption correction, based on measurements of eight reflections at $\chi = 270°$ for different azimuthal angles (Ψ scans) ($\Delta\Psi = 10°$), was made and the transmission coefficient ranged from 0.117 to 0.175 for **1** and from 0.217 to 0.127 for **2**. Fractional atomic coordinates are given in Tables 2 and 5, respectively, while selected bond lengths and angles are in Tables 3, 4 and 6, 7, respectively.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	x	y	z
Re	217(1)	2239(1)	3652(1)
C(1)	−1805(16)	2546(11)	2526(8)
O(1)	−2919(13)	2738(10)	1828(7)
C(2)	−950(15)	3235(9)	4573(8)
O(2)	−1638(12)	3876(7)	5123(6)
C(3)	−1593(17)	865(10)	3840(9)
O(3)	−2586(14)	−38(7)	3960(8)
C(7)	3214(15)	1304(10)	3952(8)
C(8)	3522(17)	2413(13)	4624(10)
C(9)	3447(16)	3398(12)	4044(11)
C(10)	3114(15)	2924(10)	3013(10)
C(11)	2964(14)	1598(9)	2942(8)
C(12)	2698(15)	775(10)	2017(8)
C(13)	2458(16)	58(10)	1286(9)
C(14)	2159(17)	−852(10)	410(8)
C(15)	499(19)	−1771(10)	147(8)
C(16)	−1282(19)	−1975(10)	642(8)
C(17)	−2869(19)	−3012(11)	336(9)
C(18)	−4355(18)	−2947(11)	965(10)
C(19)	−3768(17)	−1869(12)	1645(10)
C(20)	−1853(17)	−1278(11)	1473(8)
Mn	−1401(2)	−3072(1)	1883(1)
C(4)	835(21)	−2375(12)	2842(11)
O(4)	2245(18)	−1905(11)	3431(10)
C(5)	−2562(19)	−3894(11)	2763(10)
O(5)	−3380(18)	−4424(10)	3295(8)
C(6)	−53(22)	−4308(13)	1537(10)
O(6)	807(20)	−5110(10)	1302(9)

Additional material available from the Cambridge Crystallo-

Table 3 Selected bond lengths (Å) of compound **1**

Re–C(7)	2.308(11)	C(14)–C(15)	1.372(15)
Re–C(8)	2.292(11)	C(15)–C(16)	1.452(18)
Re–C(9)	2.291(10)	C(16)–C(17)	1.431(15)
Re–C(10)	2.307(12)	C(16)–C(20)	1.421(16)
Re–C(11)	2.325(10)	C(16)–Mn	2.172(12)
C(7)–C(8)	1.417(17)	C(17)–C(18)	1.403(19)
C(7)–C(11)	1.416(16)	C(17)–Mn	2.139(11)
C(8)–C(9)	1.406(20)	C(18)–C(19)	1.396(17)
C(9)–C(10)	1.399(19)	C(18)–Mn	2.124(11)
C(10)–C(11)	1.451(15)	C(19)–C(20)	1.417(17)
C(11)–C(12)	1.433(15)	C(19)–Mn	2.154(13)
C(12)–C(13)	1.172(15)	C(20)–Mn	2.153(12)
C(13)–C(14)	1.437(15)		

Table 4 Selected bond angles (°) of compound **1**

C(7)–Re–C(8)	35.9(4)	C(7)–Re–C(9)	59.8(4)
C(8)–Re–C(9)	35.7(5)	C(7)–Re–C(10)	59.7(4)
C(8)–Re–C(10)	59.2(5)	C(9)–Re–C(10)	35.4(5)
C(7)–Re–C(11)	35.6(4)	C(8)–Re–C(11)	59.6(4)
C(9)–Re–C(11)	60.0(4)	C(10)–Re–C(11)	36.5(4)
Re–C(7)–C(8)	71.5(6)	Re–C(7)–C(11)	72.9(6)
C(8)–C(7)–C(11)	108.2(10)	Re–C(8)–C(7)	72.7(6)
Re–C(8)–C(9)	72.1(6)	C(7)–C(8)–C(9)	108.7(11)
Re–C(9)–C(8)	72.2(6)	Re–C(9)–C(10)	72.9(6)
C(8)–C(9)–C(10)	108.2(11)	Re–C(10)–C(9)	71.7(7)
Re–C(10)–C(11)	72.4(6)	C(9)–C(10)–C(11)	108.3(11)
Re–C(11)–C(7)	71.5(6)	Re–C(11)–C(10)	71.1(6)
C(7)–C(11)–C(10)	106.6(9)	Re•C(11)–C(12)	124.3(6)
C(7)–C(11)–C(12)	127.8(10)	C(10)–C(11)–C(12)	125.5(11)
C(11)–C(12)–C(13)	176.9(12)	C(12)–C(13)–C(14)	178.1(13)
C(13)–C(14)–C(15)	124.0(11)	C(14)–C(15)–C(16)	127.9(10)
C(15)–C(16)–C(17)	123.0(10)	C(15)–C(16)–C(20)	130.9(9)
C(17)–C(16)–C(20)	106.1(11)	C(15)–C(16)–Mn	124.9(8)
C(17)–C(16)–Mn	69.4(7)	C(20)–C(16)–Mn	70.1(7)
C(16)–C(17)–C(18)	109.1(10)	C(16)–C(17)–Mn	71.9(6)
C(18)–C(17)–Mn	70.2(7)	C(17)–C(18)–C(19)	107.8(10)
C(17)–C(18)–Mn	71.4(7)	C(19)–C(18)–Mn	72.1(7)
C(18)–C(19)–C(20)	108.6(11)	C(18)–C(19)–Mn	69.8(7)
C(20)–C(19)–Mn	70.8(7)	C(16)–C(20)–C(19)	108.2(10)
C(16)–C(20)–Mn	71.6(7)	C(19)–C(20)–Mn	70.8(7)
C(16)–Mn–C(17)	38.8(4)	C(16)–Mn–C(18)	65.0(5)
C(17)–Mn–C(18)	38.4(5)	C(16)–Mn–C(19)	64.2(5)
C(17)–Mn–C(19)	63.6(5)	C(18)–Mn–C(19)	38.1(4)
C(16)–Mn–C(20)	38.3(4)	C(17)–Mn–C(20)	64.1(4)
C(18)–Mn–C(20)	64.6(4)	C(19)–Mn–C(20)	38.4(5)

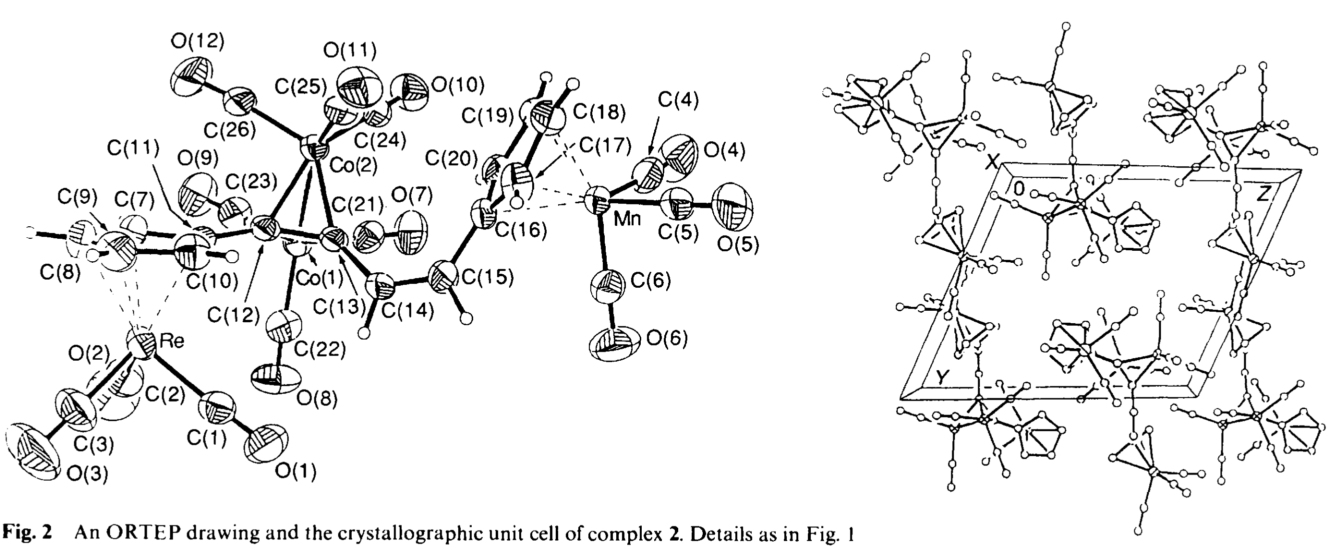


Fig. 2 An ORTEP drawing and the crystallographic unit cell of complex **2**. Details as in Fig. 1

Table 5 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	55(1)	2211(1)	4634(1)	C(14)	1156(4)	−753(4)	1919(3)
C(1)	−1327(5)	798(5)	3468(4)	C(15)	1321(5)	−1894(4)	1528(4)
O(1)	−2092(4)	−89(4)	2755(3)	C(16)	2657(4)	−2240(3)	1430(3)
C(2)	−744(6)	3246(5)	3968(5)	C(17)	3218(6)	−3083(4)	1838(4)
O(2)	−1168(6)	3908(5)	3604(5)	C(18)	4567(6)	−3116(5)	1665(4)
C(3)	−1269(7)	2308(7)	5437(5)	C(19)	4847(5)	−2322(4)	1135(4)
O(3)	−2041(6)	2370(7)	5962(4)	C(20)	3653(5)	−1784(4)	973(4)
Mn	2921(1)	−3759(1)	123(1)	Co(1)	2215(1)	1907(1)	1971(1)
C(4)	3531(6)	−3906(4)	−1026(4)	C(21)	2359(6)	1330(4)	595(4)
O(4)	3961(5)	−3987(4)	−1746(3)	O(7)	2470(5)	968(4)	−244(3)
C(5)	2742(5)	−5350(4)	−93(5)	C(22)	306(5)	1835(4)	1605(4)
O(5)	2613(5)	−6381(3)	−237(5)	O(8)	−903(4)	1761(4)	1363(4)
C(6)	1062(5)	−4116(4)	−680(4)	C(23)	2993(6)	3578(5)	2494(4)
O(6)	−150(4)	−4371(4)	−1195(4)	O(9)	3498(5)	4606(3)	2825(4)
C(7)	2415(5)	3251(4)	4978(4)	Co(2)	4286(1)	1342(1)	2954(1)
C(8)	2237(6)	3320(5)	5985(4)	C(24)	5184(5)	1104(4)	1912(4)
C(9)	1916(6)	2093(5)	5953(4)	O(10)	5742(4)	1006(4)	1273(3)
C(10)	1902(5)	1283(4)	4936(3)	C(25)	4916(5)	307(4)	3567(4)
C(11)	2223(4)	1972(3)	4306(3)	O(11)	5285(4)	−364(4)	3919(3)
C(12)	2474(4)	1521(3)	3267(3)	C(26)	5388(5)	2850(4)	3968(5)
C(13)	2208(4)	458(3)	2386(3)	O(12)	6010(5)	3787(4)	4630(4)

Table 6 Selected bond lengths (Å) of compound **2**

Re–C(7)	2.298(5)	C(11)–C(12)	1.440(6)
Re–C(8)	2.293(4)	C(12)–C(13)	1.355(5)
Re–C(9)	2.285(6)	C(12)–Co(1)	1.939(5)
Re–C(10)	2.289(5)	C(12)–Co(2)	1.958(5)
Re–C(11)	2.324(4)	C(13)–C(14)	1.459(5)
Mn–C(16)	2.177(4)	C(13)–Co(1)	1.979(5)
Mn–C(17)	2.134(5)	C(13)–Co(2)	1.965(4)
Mn–C(18)	2.118(5)	C(14)–C(15)	1.331(6)
Mn–C(19)	2.122(4)	C(15)–C(16)	1.460(7)
Mn–C(20)	2.142(4)	C(16)–C(17)	1.417(7)
C(7)–C(8)	1.408(8)	C(16)–C(20)	1.414(7)
C(7)–C(11)	1.441(6)	C(17)–C(18)	1.407(8)
C(8)–C(9)	1.421(9)	C(18)–C(19)	1.399(9)
C(9)–C(10)	1.397(7)	C(19)–C(20)	1.426(7)
C(10)–C(11)	1.423(7)	Co(1)–Co(2)	2.464(1)

Table 7 Selected bond angles (°) for compound **2**

C(7)–Re–C(8)	35.7(2)	C(7)–Re–C(9)	59.8(2)
C(8)–Re–C(9)	36.2(2)	C(7)–Re–C(10)	59.7(2)
C(8)–Re–C(10)	59.7(2)	C(9)–Re–C(10)	35.6(2)
C(7)–Re–C(11)	36.3(1)	C(8)–Re–C(11)	60.2(2)
C(9)–Re–C(11)	60.0(2)	C(10)–Re–C(11)	35.9(2)
C(16)–Mn–C(17)	38.3(2)	C(16)–Mn–C(18)	64.5(2)
C(17)–Mn–C(18)	38.7(2)	C(16)–Mn–C(19)	64.5(2)
C(17)–Mn–C(19)	64.6(2)	C(18)–Mn–C(19)	38.5(2)
C(16)–Mn–C(20)	38.2(2)	C(17)–Mn–C(20)	64.5(2)
C(18)–Mn–C(20)	64.8(2)	C(19)–Mn–C(20)	39.1(2)
Re–C(7)–C(8)	71.9(3)	Re–C(7)–C(11)	72.8(2)
C(8)–C(7)–C(11)	108.7(5)	Re–C(8)–C(7)	72.4(2)
Re–C(8)–C(9)	71.6(3)	C(7)–C(8)–C(9)	107.8(4)
Re–C(9)–C(8)	72.2(3)	Re–C(9)–C(10)	72.4(3)
C(8)–C(9)–C(10)	108.1(5)	Re–C(10)–C(9)	72.1(3)
Re–C(10)–C(11)	73.4(3)	C(9)–C(10)–C(11)	109.6(4)
Re–C(11)–C(7)	70.9(3)	Re–C(11)–C(10)	70.7(3)
C(7)–C(11)–C(10)	105.8(4)	Re–C(11)–C(12)	128.2(3)
C(7)–C(11)–C(12)	126.0(4)	C(10)–C(11)–C(12)	127.8(4)
C(11)–C(12)–C(13)	141.0(4)	C(11)–C(12)–Co(1)	138.4(3)
C(13)–C(12)–Co(1)	71.4(3)	C(11)–C(12)–Co(2)	129.6(3)
C(13)–C(12)–Co(2)	70.1(3)	Co(1)–C(12)–Co(2)	78.4(2)
C(12)–C(13)–C(14)	134.7(4)	C(12)–C(13)–Co(1)	68.2(3)
C(14)–C(13)–Co(1)	130.5(3)	C(12)–C(13)–Co(2)	69.5(2)
C(14)–C(13)–Co(2)	145.3(3)	Co(1)–C(13)–Co(2)	77.3(1)
C(13)–C(14)–C(15)	131.1(4)	C(14)–C(15)–C(16)	127.3(4)
C(15)–C(16)–Mn	128.5(2)	C(17)–C(16)–Mn	69.2(3)
C(15)–C(16)–C(17)	124.5(5)	C(20)–C(16)–Mn	69.5(2)
C(15)–C(16)–C(20)	128.1(4)	C(17)–C(16)–C(20)	107.4(4)
C(16)–C(17)–Mn	72.5(3)	C(18)–C(17)–Mn	70.1(3)
C(16)–C(17)–C(18)	108.4(5)	C(17)–C(18)–Mn	71.3(3)
C(19)–C(18)–Mn	70.9(3)	C(17)–C(18)–C(19)	108.3(5)
C(18)–C(19)–Mn	70.6(2)	C(20)–C(19)–Mn	71.2(2)
C(18)–C(19)–C(20)	107.9(5)	C(16)–C(20)–Mn	72.2(2)
C(19)–C(20)–Mn	69.7(2)	C(16)–C(20)–C(19)	107.9(5)
C(12)–Co(1)–C(13)	40.4(2)	C(12)–Co(1)–Co(2)	51.1(1)
C(13)–Co(1)–Co(2)	51.1(1)	C(12)–Co(2)–C(13)	40.4(1)
C(12)–Co(2)–Co(1)	50.4(1)	C(13)–Co(2)–Co(1)	51.6(1)

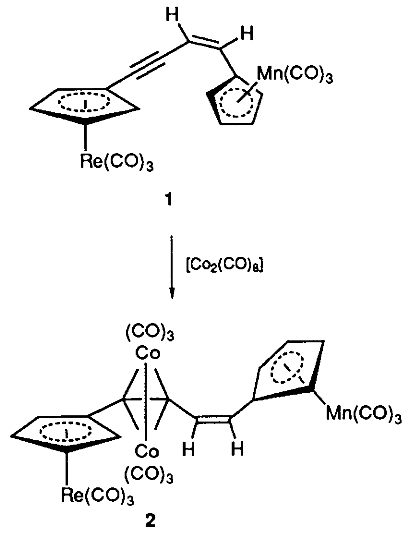
graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The result of the X-ray structure determination carried out on compound **1** lends *a posteriori* support to the hypothesis outlined in the Introduction of the possibility of the (*Z*)-enyne linkage favouring proximity of the two metal centres (Fig. 1). In fact the most striking structural characteristic of complex **1** is that the torsion angle of the C(12)–C(13)–C(14)–C(15) chain (54.7°) defines a *gauche* relative position of the two C_5H_4 rings with a dihedral angle of 61.7°. The geometrical parameters of the chain itself connecting the two cyclopentadienyl units are quite normal and differ insignificantly from standard values.[5] This pronounced bending of the C(14)–C(16) chains is indicative of a large degree of rotational freedom of the two cyclopentadienyl moieties of the (*Z*)-enyne linkage. Moreover, the torsion angle at the C(13)–C(16) (3.3°) and the C(14)–C(20) (3.6°) portions of the bridge, and the C(15)–C(16)–C(20) and C(15)–C(16)–C(17) angles (130.9 *vs.* 123.0°) show that there is no evident restriction imposed by the conjugation.

Although the interatomic distance between the two metal centres is sensibly shorter than that found in other related heterobimetallic complexes[2b] (6.01 *vs.* 7.6 Å), it will not allow direct bond interaction between the metal centres. On the other hand, because of the degree of freedom allowed by the enyne linkage, it is reasonable to assume that conformational change in the ligand framework could take place, leading to interaction of the ancillary ligands on one metal with the other metal. By appropriate choice of the two metals, new reaction patterns could be explored for ancillary ligands simultaneously interacting with two different metal centres.

In the solid state the complex exists as discrete, well separated molecules (Fig. 1) which are held together by van der Waals



Scheme 1

forces. The shortest non-hydrogen intermolecular contacts are 3.11 Å for O ··· O, 3.24 Å for C ··· O and 3.25 Å for C ··· C approaches. The Re and Mn atoms have the usual 'piano stool' co-ordination characteristic of monocyclopentadienyl $[\mathrm{M}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{L_3}]$ (L = monodentate two-electron donor) with a substantially undistorted C_{3v} symmetry of the $\mathrm{Re(CO)_3}$ and $\mathrm{Mn(CO)_3}$ fragments, the bond angles (O)C–M–C(O) being in the range 89.5–93.2°. The distances of the Re and the Mn from the centroids of the pertinent $\mathrm{C_5H_4}$ ring are 1.964 and 1.780 Å, respectively, in excellent agreement with the values found in $[\mathrm{Re}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]$[6] and $[\mathrm{Mn}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]$.[7] Moreover, a comparison of all the structural parameters shows that the presence of the chain results in insignificant changes relative to the structures of $[\mathrm{Re}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]$ and $[\mathrm{Mn}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3]$. On the other hand, vibrational corrections[8] to be applied to the bond lengths are in the range 0.002–0.007 Å which is within the standard deviations.

Structure **1** was then further elaborated by reaction with $[\mathrm{Co_2(CO)_8}]$. The typical dicobalt tetragonal pyramidal adduct **2** was quantitatively formed after stirring the compound with a slight excess of $[\mathrm{Co_2(CO)_8}]$ in benzene (Scheme 1). In contrast to **1**, compound **2** was easily crystallized from thf–pentane, affording good X-ray-quality crystals. An ORTEP drawing of compound **2** is shown in Fig. 2.

The addition of the $\mathrm{Co_2(CO)_6}$ unit to the C(12)–C(13) triple bond of **1** produces complex **2**, in which the overall conformation is modified (Fig. 2). The Re ··· Mn separation shifts from 6.01 to 9.05 Å and the two $\mathrm{C_5H_4}$ centroids are placed at a distance of 7.11 Å (6.39 Å in **1**). The C(12)–C(13)–C(14)–C(15) torsion angle goes from 54.7 to 136.1°, so that the *gauche* position of this part is replaced by an *anticlinal* one, while the dihedral angle between the $\mathrm{C_5H_4}$ planes remains substantially unmodified (64.5 *vs.* 61.7° in **1**).

Noteworthy is the fact that the attachment of the $\mathrm{Co_2(CO)_6}$ unit to the alkyne moiety formally changes the hybridization of the C(12) and C(13) carbons from sp to sp^3, so that the linear array of the C(11)–C(12)–C(13)–C(14) tract of the carbon chain in **1** is markedly bent in **2**. Supposing that in solution free rotation is possible in the C(11)–C(12), C(13)–C(14) and C(15)–C(16) parts of the carbon chain, this effect could facilitate bringing the two metal centres closer together.

The Co(1)–Co(2) distance (2.464 Å) is practically the same as that found in $[\mathrm{PhC{-}(OC)_3Co{-}Co(CO)_3CPh}]$ (2.47 Å)[9] and $[\mathrm{Bu^tC{-}(OC)_3Co{-}Co(CO)_3CBu^t}]$ (2.463 Å),[10] while it is remarkably shorter than that in $[\mathrm{Co_2(CO)_8}]$ (2.524 Å).[11] Comparison of some relevant data for the $\mathrm{RC{-}(OC)_3Co{-}Co(CO)_3CR}$ portions of the three complexes confirms that they differ very little and in particular superimposition of **2** with $[\mathrm{Bu^tC{-}(OC)_3Co{-}Co(CO)_3CBu^t}]$ shows a weighted root-mean-square (r.m.s.) deviation of only 0.163 Å. The major distortion from an octahedral arrangement around each cobalt atom mainly derives from the narrow C(12)–Co(1)–C(13) and C(12)–Co(2)–C(13) angles (both 40.4°) and, as found in **1**, the crystal of **2** has a normal packing without any intermolecular contacts (Fig. 2).

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