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Spectroscopic Properties and Crystal Structure of Tricarbonylcobalta-2,5-diphenyl-3,4-dimethylcyclopenta-2,4-dienetricarbonylmanganese, $[CoMn(CO)_6(Ph_2C_4Me_2)]$

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In an earlier paper [1] we reported the syntheses of the tetrahedrane products $[CoMn(CO)_7(RC_2R^1)]$ via facile thermal reactions of internal alkynes with $[CoMn(CO)_9]$. We now report that the deep red compound $[CoMn(CO)_6(Ph_2C_4Me_2)]$ (I), which has a 'ferrole' structure [2], is formed via the reaction, in refluxing hexane, of $[CoMn(CO)_9]$ or $[CoMn(CO)_7(PhC_2Me)]$ with the appropriate molar ratio of methylphenylacetylene.

Ferrole complexes are relatively common products of reactions of iron carbonyls with alkynes [3]. A few analogous complexes, containing osmium [4, 5], rhodium [6], iridium [7, 8] and rhenium [9] in place of iron are known. Only two iron/nickel [10] and cobalt/tungsten [11] mixed metal ferrole systems have been structurally characterized. The spectroscopic identification of $[FeRu(CO)_6(Ph_4C_4)]$ is reported [12]. Our new compound $[CoMn(CO)_6(Ph_2C_4Me_2)]$ (**I**) is isoelectronic with analogous di-iron ferroles, but it shows nevertheless significant structural differences which are described below.

Compound **I** was purified by column chromatography on silica followed by recrystallization from a chloroform/hexane solvent mixture. The mass spectrum of **I** showed a weak signal for the parent ion (P_c for $CoMnC_{24}H_{16}O_6$ = 514.3; P_o = 514), and the sequential loss of six carbonyl groups. The base peak corresponded to $[CoMn(Ph_2C_4Me_2)]^+$. The infrared spectrum (ν_{CO} region) consisted of six medium to strong bands in the region for terminally bound CO, at 2088, 2046, 2027, 2003, 1947 and 1933 cm^{-1}.

The ^{13}C NMR spectrum of compound **I** consisted of two resonances, at δ = 225.4 and 198 ppm, attributable to the carbonyl groups of the $Co(CO)_3$ moiety; a single resonance at δ = 181 ppm due to the equivalent carbonyls of the π-bonded $Mn(CO)_3$ group; two singlets for the C(7), C(10) (at δ = 148.3) and the C(8), C(9) (at δ = 120.4) pairs of ring carbon atoms; and resonances due to the phenyl and methyl substituents (see Figs. 1, (a) and (b) for structure and numbering scheme). The above assignments for $[CoMn(CO)_6(Ph_2C_4Me_2)]$ are consistent with reported analyses of the ^{13}C NMR spectra of several related $[Fe_2(CO)_6(R_2C_4R^1{}_2)]$ derivatives [13–15].

A single crystal of compound **I** was grown from a chloroform/hexane solution. Crystal data: $CoMnC_{24}H_{16}O_6$, M = 514.3, monoclinic, space group $P2_1/c$, a = 16.308(3), b = 8.875(2), c = 15.574(4) Å, β = 93.44(2)°, Z = 4, V = 2250 $Å^3$, D_c = 1.516, D_o = 1.53 g cm^{-1}, μ(Mo Kα) = 13.1 cm^{-1}. Final R and R_w values were 0.0334 and 0.0428 for 2373 observed reflections [$I > 3\sigma(I)$] of 3939 independent reflections measured on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation.

The intensity data were corrected for Lorentz, polarization and absorption effects. The positions of the metal atoms were located from a Patterson map, and the non-hydrogen atoms were located from a series of difference Fourier synthesis interspersed with least-squares refinement cycles. Scattering

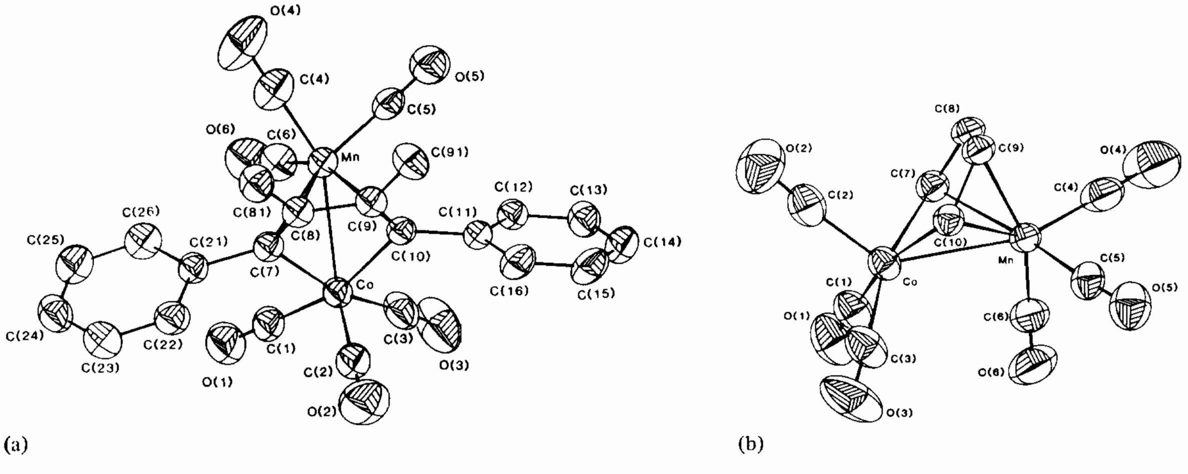

Fig. 1. Structure and atom numbering scheme for $[CoMn(CO)_6(Ph_2C_4Me_2)]$ (I).

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factors and anomalous dispersion corrections were obtained from the literature [16]. Computer programs were run on a VAX 11/750 [17].

The final atomic coordinates for the non-hydrogen atoms of [CoMn(CO)$_6$(Ph$_2$C$_4$Me$_2$)] are given in Table I. Thermal parameters, the calculated hydrogen atom coordinates, and a list of structure factors have been deposited with the Editor-in-Chief and are also available from the authors.

ORTEP diagrams of compound **I** are shown in Figs. 1, (a) and (b). The bond parameters are given in Table II. The structure consists of a substituted cobaltacyclopentadienyl ring which is bound to the Mn(CO)$_3$ fragment by a metal–metal bond and by 4-electron π bonding. The methylphenylacetylene precursors of the cyclopentadienyl ring are linked in a head to head fashion, and the C(7) and C(10) carbon atoms which bear phenyl substituents are σ-bonded to the Co(CO)$_3$ moiety. An 18-electron count is established for both metal centres. The Co–Mn bond length in compound **I** (2.5488(8) Å) is shorter than the sum of the covalent radii (2.65 Å [18]) and is similar to the value of 2.561(1) Å found in [(MeCp)MnCo$_2$(Me$_5$C$_5$)$_2$(CO)$_4$] [19]. A shorter metal–metal distance of 2.505(1) Å is observed in the closely related ferrole [Fe$_2$(CO)$_6$(Ph$_4$C$_4$)] [20].

TABLE I. Atom Coordinates (x10^4) for CoMn(CO)$_6$(MeC$_2$Ph)$_2$

Atom	*x*	*y*	*z*
Co	1851.5(3)	5311.1(5)	4384.2(3)
Mn	2933.1(3)	7311.8(6)	4765.0(3)
C(1)	863(2)	6219(4)	4145(2)
O(1)	254(2)	6786(4)	3993(2)
C(2)	1610(2)	3573(4)	4904(3)
O(2)	1496(2)	2480(3)	5252(2)
C(3)	1878(2)	4736(5)	3259(3)
O(3)	1846(2)	4371(5)	2566(2)
C(4)	3329(3)	8803(4)	5438(2)
O(4)	3583(3)	9746(4)	5887(2)
C(5)	3779(2)	7555(4)	4090(2)
O(5)	4335(2)	7731(3)	3682(2)
C(6)	2294(2)	8579(4)	4122(2)
O(6)	1895(2)	9393(4)	3708(2)
C(7)	1992(2)	6432(4)	5480(2)
C(8)	2727(2)	6101(4)	5954(2)
C(81)	2913(2)	6595(4)	6875(2)
C(9)	3318(2)	5315(4)	5485(2)
C(91)	4157(2)	4944(4)	5882(2)
C(10)	3041(2)	4970(4)	4625(2)
C(11)	3518(2)	3946(4)	4089(2)
C(12)	3707(2)	4281(4)	3251(2)
C(13)	4155(2)	3294(5)	2775(2)
C(14)	4422(3)	1948(5)	3133(3)
C(15)	4237(3)	1578(4)	3953(3)
C(16)	3782(3)	2571(4)	4430(2)
C(21)	1279(2)	7111(4)	5910(2)
C(22)	883(2)	6257(4)	6504(2)
C(23)	209(2)	6827(5)	6900(2)
C(24)	−79(2)	8232(5)	6699(3)
C(25)	302(3)	9093(5)	6119(3)
C(26)	984(2)	8544(4)	5271(2)

TABLE II. Bond Distances (A) and Angles (deg) for CoMn(CO)$_6$(MeC$_2$Ph)$_2$

Co–Mn	2.5488(8)
Co–C(1)	1.823(4)
Co–C(2)	1.797(4)
Co–C(3)	1.829(4)
Co–C(7)	1.977(3)
Co–C(10)	1.977(3)
Mn–C(4)	1.785(4)
Mn–C(5)	1.798(4)
Mn–C(6)	1.798(4)
Mn–C(7)	2.100(3)
Mn–C(8)	2.185(3)
Mn–C(9)	2.170(3)
Mn–C(10)	2.098(3)
C(7)–C(21)	1.504(5)
C(7)–C(8)	1.401(5)
C(8)–C(81)	1.513(5)
C(8)–C(9)	1.426(5)
C(9)–C(10)	1.423(5)
C(9)–C(91)	1.506(5)
C(10)–C(11)	1.486(5)
C(1)–O(1)	1.127(5)
C(2)–O(2)	1.132(5)
C(3)–O(3)	1.124(5)
C(4)–O(4)	1.52(5)
C(5)–O(5)	1.149(5)
C(6)–O(6)	1.145(5)
Co–C(1)–O(1)	179.5(4)
Co–C(2)–O(2)	176.6(4)
Co–C(3)–O(3)	176.0(4)
Mn–C(4)–O(4)	178.6(4)
Mn–C(5)–O(5)	177.7(4)
Mn–C(6)–O(6)	179.2(4)
Co–C(7)–C(8)	113.7(2)
Co–C(7)–C(21)	122.2(2)
Co–C(10)–C(9)	113.5(2)
Co–C(10)–C(11)	121.9(2)
Mn–C(7)–C(8)	74.2(2)
Mn–C(7)–C(21)	134.2(2)
Mn–C(10)–C(9)	73.3(2)
Mn–C(10)–C(11)	135.6(2)
C(8)–C(7)–C(21)	120.6(3)
C(81)–C(8)–C(7)	123.7(3)
C(81)–C(8)–C(9)	121.6(3)
C(91)–C(9)–C(8)	121.5(3)
C(91)–C(9)–C(10)	124.8(3)
C(9)–C(10)–C(11)	120.9(3)

The three terminal carbonyl groups of the Mn(CO)$_3$ have similar Mn–C bond lengths and are equivalent on the NMR time scale at temperatures down to −60 °C. The three carbonyls of the Co(CO)$_3$

moiety, however, have different Co–C bond distances and exhibit two ^{13}C NMR signals at room temperature. The two carbonyls which are *trans* to the Co–C σ-bonds of the cobaltacyclopentadienyl ring have the longer Co–C bonds. The more closely bound carbonyl is essentially at right angles to the plane of the metallocyclic ring. Similar effects have been noted in analogous ferrole compounds [14, 21].

The C–C bond lengths of the cyclopentadienyl ring of compound **I** are nearly identical, as is found in several ferrole structures [14]. Thorn and Hoffmann [22] have attributed this 'bond levelling' effect to back donation of electron density from the π-bonded metal to the LUMO π^* orbital of the diene fragment.

The 'inner' carbon atoms, C(7) and C(10), have slightly shorter bond distances to Mn than the 'outer' carbons, C(8) and C(9). A similar pattern is observed in ferrole structures [10, 22].

In the solid state, ferrole complexes adopt a 'sawhorse' (carbonyls eclipsed) or a 'non-sawhorse' (carbonyls staggered) geometry, the latter being found in most cases [22]. The two structures are interconverted by a 60° rotation of the π-bonded $Fe(CO)_3$ fragment. In the non-sawhorse geometry (the lower in energy by $\approx$0.2 eV [22]), one of the carbonyls of the π-$Fe(CO)_3$ group occupies a semi-bridging position with respect to the iron atom of the FeC_4 ring, apparently in order to relieve coordinative unsaturation at that centre. In $[CoMn(CO)_6(Ph_2C_4Me_2)]$, the Co centre is coordinatively saturated, thus precluding the non-sawhorse configuration. The actual structure is in fact intermediate between the sawhorse and non-sawhorse geometries; two dihedral angles (20° and 26°) between Mn–Co–carbonyl and Co–Mn–carbonyl planes are observed, due to asymmetry in the disposition of the carbonyl ligands on cobalt.

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