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Review

MANGANESE CARBONYL AND ORGANOMETALLIC COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

CLIVE E. HOLLOWAY, Department of Chemistry, York University, 4700 Keele St., Downsview, Ontario, M3J 1P3, Canada

MILAN MELNIK, Department of Inorganic Chemistry, Slovak Technical University, CS 812 37, Bratislava, Czechoslovakia

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0. ABBREVIATIONS

aac	(allylamino)carbene
ac	acetate
acac	acetylacetonato
acf	3-acetyl-4,5-dihydrofuran-2-yl
acn	acetonitrile
acp	2-acetylphenyl
acpr	acetylpyrrolyl
adm	aziridinylmethyl
ak	anthronylketone
bcpf	bis(cymantrenylphenyl)fulvene
bcpp	bis(cymantrenylphenyl)cyclopentene
bdmp	1-tert-butyl-3,4-dimethylphosphole
bhp	(2-benzylidenehydrazonomethyl)phenyl
bpy	2,2'-bipyridine
bu-iae	1-(tert-butylimino)-2-(tert-butylamine)ethane
c	cubic
cbdcp	cyclobuta[1,3-a:3,4-a']dicyclopentane
cp	cyclopentadienyl
cp*	methylcyclopentadienyl
cp-ac	acetylcyclopentadienyl
cp-bz	benzoylcyclopentadienyl
cp-df	1-{α-(N,N'-dimethylamino)ethyl}-2-formylcyclopentadienyl
cp-mc	-methylcyclopentadienylcarboxylate
cp-tm	{6,7-(α,α,δ,δ-tetramethylcyclohexene)cyclopentadienyl}- -propanoic acid
dac	1,1-diphenyl-1-arsa-cyclopentane
dam	dimethyldiazomalonate
dca	dicyclohexylallenylidene
dep	1-diethylphosphonato-2-phenylethylene
dik	see original literature, methylene linkage to metal
dmap	1,3-bis(dimethylarsino)propane
dmb	2-(dimethylaminomethyl)phenyl
dmp	3,4-dimethylphospholyl
dmpe	1,2-bis(dimethylphosphino)ethane
dmpz	3,5-dimethyl-1-pyrazole
dop	1-syn-(1',2',-dihydro-2'-oxo-1'-oxa-azulen-3'-yl)- -η^5-cyclopentadienyl
dopc	2,2'-diphenyl-1-oxa-2-phospha-cyclobutane
doph	2,2'-diphenyl-1-oxa-2-phospha-cycloheptane
dopo	2,2'-diphenyl-1-oxa-2-phospha-cyclohexa-5-one
dpac	diphenylacetate
dpc	1,1'-diphenyl-1-phospha-cyclobutane
dph	1,1'-diphenyl-1-phospha-cycloheptane
dpch	1,1'-diphenyl-1-phospha-cyclohexane
dpe	1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutane
epb	2-ethyl-1-phenylborole
fyfars	1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutane
hdd	2,4-hexadien-2,5-diyl
m	monoclinic
mbt	dimercaptobenzothiazolate
mdpa	bis(diphenylarsino)methane
mdpc	3-methyl-1,1-diphenyl-1-phospha-cyclopentane
mdpp	bis(diphenylphosphino)methane
mes	mesityl
min	2-methylindolyl
mopp	2-(1',2',-dimethyloxopropenyl)phenyldiphenylphosphine
mpc	3,4-dimethylphospha-cymantrene
msp	(methylsulphidomethyl)phenyl
mtpc	3,3-dimethyl-4-thia-3-phospha-cyclopentadiene- -1,2-dimethyl ester

1-np	1-naphthyl
obdp	(σ-3-oxobutylphenyl)diphenylphosphine
or	orthorhombic
pcr	picrate
pfp	2-(N-phenylformimidoyl)phenyl
phen	1,10-phenanthroline
pmte	N-isopropyliden-S-methyldithiocarbazinate
popc	2,2-diphenyl-1-oxa-2-phospha-cyclohexane
ppn	bis(triphenylphosphine)nitrogen(+)
rh	rhombohedral
tg	tetragonal
thf	tetrahydrofuran
tmeda	N,N,N',N'-tetramethylethylenedianime
tmi	tetramethyl-α-diimine
tmdt	2,4,7,9-tetramethyl-1,3,7,9-decatetraene
tmpo	2,2,6,6-tetramethylpiperidinyl-1-oxo
top	2-(bis-p-tolylphosphino)-5-methylphenyl
topc	2,2,5,5-tetramethyl-1-oxa-2-phospha-cyclohexane
tpbp	2,2,4,4-tetraphenyl-1-H-benzodiphospherinyl
tpe	2-thiophenoxyethoxy
tpp	α,β,γ,δ-tetraphenylporphinate
tr	triclinic
trg	trigonal

1. INTRODUCTION

Manganese, one of the more abundant of the heavier metallic elements, appears to be essential to life in trace amounts, and is known to be involved in enzymatic reactions including the formation of glucosamine-serine linkages, the synthesis of cartilage mucopolysaccharides, the action of pyruvate carboxylase and the utilization of glucose [1].

The element is typified by multiple oxidation states, and its compounds have had wide use in catalysis. Organometallic compounds have been summarized in annual reports [2], and coordination compounds have been reviewed [3]. The purpose of this review is to draw together and correlate the known structural data for all the various manganese carbonyl and organometallic compounds published up to 1986 (volume 105 of Chemical Abstracts).

The structures have been classified according to the coordination number of the manganese, subdivided into monomers, oligomers and polymers. The compounds are listed in order of increasing coordination number, increasing complexity of the coordination sphere and increasing atomic number of the principal ligating atom. Where possible the estimated standard deviations of structural parameters from the mean value are given in parenthesis.

2. MANGANESE CARBONYL COMPOUNDS

(A) Mononuclear Compounds

1. Coordination numbers four and five.

Four is the lowest coordination number found for mononuclear manganese carbonyl compounds, there being only one example $\{(PPh_3)_2N\}$ $[Mn(CO)_2(NO)_2]$ [5] This red-orange product has tetrahedral geometry around the Mn(-1) atom, with

Table 1 Structural data for manganese carbonyl compounds with coordination number four and five

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	L_{eq}-M-L_{eq} L_{eq}-M-L_{ax} L_{ax}-M-L_{ax} [°]	Ref
$\{(PPh_3)_2N\}[Mn^{-1}(CO)_2(NO)_2]$	m	$P2_1/a$	4	2189(5) 919.4(3) 1749.5(3)	 96.25(2) 	MnN_2C_2	N[b] 171.9(6,12) C 174.8(6,3)	109.5(2,2.2)	5
$[Mn^{-1}(CO)_5][fac\text{-}Mn^{1}(CO)_3(NH_3)_3]$	or	Pnma	4	1245.1 953.4 1227	 	MnC_5	C 176.2(8,10) C_{ax} 179.2(11,10)	119.9(3,5.3) 90.1(4,2.9) 178.9(4)	6
						MnN_3C_3	N 209.6(7,1)	85.9(2,7)[c]	
$Mn^{1}(CO)_5]_2[Ni(phen)_3]$[d,e]	tr	P1	2	1361.8(5) 1432.5(5) 1239.9(8)	102.16(4) 113.22(4) 98.46(3)	MnC_5	C 180.4(11,14) C_{ax} 181.7(11,15)	120(4,5 90(4,1.5) 178.2(3)	7
						MnC_5	C 179.1(10,19) C_{ax} 182.3(11,8)	120(4,3.4) 90(4,1.6) 178.6(4)	
$Mn(CO)_4(NO)$[f]	m	C2/c	4	1172(3) 674(2) 965(2)	 107.8(1) 	MnC_4N	N 179.7(13) C 185.1(8)(2x) C_{ax} 188.6(8)(2x)	120(3,1.1) 90(4,2/0) 179.6(7)	8
$(Ph_4)[Mn^{-1}(CO)_4PPh_3]$[g]	m	$P2_1/c$	4	1073.5(3) 1741.2(4) 2084.7(8)	 99.16(2) 	MnC_4P	C 179.5(7,6) C_{ax} 179.7(6) P_{ax} 224.8(2)	120(3,6.8) 90(3,5.2) 172(2)	9
$[Mn^{1}(C0)_3(NSiMe_3\{P(OPh)\text{-}$[d] $.[N(SiMe_3)_2\}]$	m	$P2_1/c$	8	2122.3(4) 1736.3(4) 1785.9(4)	 98.63(2) 	MnC_3N_2	C 178.2(9,5) N 202.7(5,14) C_{ax} 174.8(8)	[h]	10
						MnC_3N_2	C 1.766(9,15) N not given C_{ax} 177.5(8)		

Table 1, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromo-phore	M-L [pm]	L_{eq}-M-L_{eq} L_{eq}-M-L_{ax} L_{ax}-M-L_{ax} [°]	Ref
$Mn^{0}(CO)_5(tmpo)$	m	$P2_1/c$	4	628.5(2) 1480.6(7) 1484(6)	 9029(31) 	MnC_3NO	C 181.5(4) N 198.1(3) O 183.9(3) C_{ax} 178.1(4,6)	i	11
$Mn(CO)_2(NO)(PPh_3)_2$	or	Pbca	8	1815(8) 1707(8) 2186(11)	 	MnC_2P_2N	C 177(2,2) N 173(1) P_{ax} 227.9(5,1)	120(7,1.3) 90(5,4.5) 170.2(2)	12

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The value of C-Mn-C angle; C-Mn-N = 92.5(3,1.7) and 177.8(3,1.2)°; N-Mn-N = 85.9(2,7)°.
d There are two crystallographically independent molecules;
e at 150(2)K.
f at 163K.
g at 238K.
h The C_{ax}-Mn-C_{ax} = 84.4(4)°; N_{eq}-Mn-N_{eq} = 74.4(2)°; C_{eq}-Mn-C_{ax} = 88.9(4,3)°.
i The C-Mn-O = 105.1(1) and 135.4(2,2)°; C-Mn-N = 112.1(2) and 148.3(2)°.

Mn-C bond distances of 174.5 and 175.0(6) pm, and Mn-N bond distances of 170.7(5) and 173.0(6) pm (Table 1).

Crystallographic and structural data for five coordinate manganese carbonyl compounds are given in Table 1. There are two types of geometry, trigonal bipyramid and square pyramid. Of the latter there is only one example, $Mn(CO)_3(NSiMe_3)_2\{P(OPh)[N(SiMe_3)_2]\}$ [10], where the central MnC_3N_2 skeleton corresponds to a distorted square-pyramidal environment. In all the other examples the trigonal bipyramidal geometry occurs, for which the crystal structure of deep red $(Ph_4P)[Mn(CO)_4PPh_3]$ [9] is shown in Figure 1 as a representative example. The CO and PPh_3 ligands are in axial sites (Mn-C = 179.7(6) pm and Mn-P = 224.8(2) pm, and the remaining three CO ligands occupy equatorial coordination sites (Mn-C = 180.1, 178.9 and 179.6(6) pm). Except for one example $Mn(CO)_3$(tmpo) [11], only unidentate ligands are involved in the five coordination of manganese listed in Table 1.

The oxidation states found for the manganese occur in the order zero <-1 <+1. Two crystallographically independent molecules, differing by degree of distortion, have been found for $[Mn(CO)_5]^-$ [7] and $Mn(CO)_3NSiMe_3)_2\{P(OPh)(N(SiMe_3)\}_2$ [10] and they are examples of distortion isomerism [4].

2. Coordination number six

The overwhelming majority of manganese coordination compounds are six coordinate and the carbonyl derivatives follow the same trend. From the data in Table 2 it can be seen that there are no examples of the regular (O_h) octahedron, however, the three principal types of distortion for the octahedron, tetragonal, rhombic and trigonal are all found. The crystal structure of colourless $Mn(CO)_2[OC_6H_4OP(O)]$ [8] is shown in Figure 2 as a representative example. The metal atom has four equatorial carbonyl ligands (Mn-C = 186.5(7.9)pm), one axial carbonyl (Mn-C = 186.7(6)pm) and an axial 1,3,2-benzodioxaphosphole-2-oxide (Mn-P = 230.7(2)pm).

The data in Table 2 show that the predominant oxidation state of the manganese is +1. There are no examples with all six ligands equivalent. There are several occurrences of isomerism, for example colourless $Mn(CO)_2[P(OMe)_2Ph]_4](PF_6)$ [26] was found in cis and trans isomeric forms. There are another three examples: α- and ß-$HMn(CO)_5$ [13, 14]; fac- and mer-$Mn(CO)_3Br[P(OMe)_2Ph]_2$ [35]; cis and trans $[Mn(CO)_2(phen)\{P(OMe)_3\}](C10_4)$ [41]; all of which differ mostly in degree of distortion. Two crystallographically independent molecules, differing in degree of distortion, have been found for mer-$Mn(CO)_3Br[P(OMe)_2Ph]_2$ [35] and $Mn(CO)_3Cl[P(Ph)_2(C_5H_7N_2)]$ [38] and are further examples of distortion isomerism [4]. The fac- and mer- $Mn(CO)_3Br[P(OMe)_2Ph]_2$ derivatives mentioned above are unique examples of this phenomenon.

Table 2 Structural data for mononuclear manganese carbonyl compounds with a coordination number six[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore		M-L [pm]	OC-M-CO cis-[°] trans-[°]	Ref
α-$HMn^{I}(CO)_5$[c]	m	I2/a	8	1218(2) 635(1) 1920(3)	 93.3(5) 	MnC_5H	C[b] H	183.6(9,16) not located	93(4,4.4) 166.4(4,1)	13
ß-$HMn^{I}(CO)_5$[c]	m	C2/c	8	1216(3) 628(2) 1934(4)	 91.2(5) 	MnC_5H	C H	184.7(17,23) not located	93(7,4.8) 166.5(7,2.2)	14
						MnC_5H[d]	C H	184.7(13,14) 160.1(16)	93.1(5,5.4)[e] 165.7(6,1.7)	
$Mn^{I}(CO)_5(F_3CCOO)$	m	$P2_1/n$	4	692.7(2) 1345.4(4) 1160.3(3)	 92.11(2) 	MnC_5O	C O	187.4(5,59) 203.1(2)	90.7(2,2.4)[f] 176.9(2,1.5)	15
$Mn^{I}(CO)_5Cl$	or	Pnma	4	1154(2) 1152(2) 595(1)		MnC_5Cl	C C_{ax} Cl_{ax}	189.3(6,1) 180.7(9) 236.7(4)	90.8(3,1.8)[g] 176.4(3)	16
$Mn(CO)_5\{o\text{-}HOC_6H_4O)_2P(O)\}$	tg	$I4_1/a$	16	2514.5(10)		MnC_5P	C P	185.3(6,17) 229.7(2)	91.2(3,4.9)[h1] 174.8(3,1)	17
$Mn(CO)_5\{OC_6H_4OP(O)\}$	tr	P1	2	675.3(2) 881.8(3) 1200.4(4)	106.79(2) 105.37(2) 98.82(2)	MnC_5P	C P	186.5(7,9) 230.7(2)	91.4(3,2.4)[h2] 174(3,3)	18
$Mn^{I}(CO)_3(CNCH_3)_3Br$	tr	P1	2	890(2) 1090.7(3) 615.5(2)	97.93(1) 108.45(1) 81.86(1)	MnC_5Br	OC C OC_{ax} Br_{ax}	183.5(12,20) 197.1(12,21) 178.9(11) 253.7(2)	90.8(4)[i1]	19
$Mn^{I}(CO)_3(CNPh)_2Br$	m	$P2_1/n$	4	1803 593 168.3	 107.33 	MnC_5Br	OC C Br	174(6,3) 193(4,1) 252.7(8)	92(2,3)[i2]	20

Table 2, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	OC-M-CO cis-[°] trans-[°]	Ref
$[Mn^1(CO)_2(CNPh)(CNBu)(phen)].ClO_4$	m	$P2_1/n$	4	1534.3(3) 1291(3) 1451.1(3)	 105.51(2) 	MnC_4N_2	N 205.5(5,19) OC 178.7(8) BuNC 186.2(6) $PhNC_{ax}$ 196.4(6) OC_{ax} 182.3(7)	89(3)[j1]	21
$[Mn^1(CO)_3(CNBu)phen)]ClO_4$	tr	P1	2	1824.6(3) 1355.4(2) 945.2(2)	111.53(2) 118.94(2) 118.63(2)	MnC_4N_2	N 206.4(4,4) OC 181.3(7,7) OC_{ax} 184.6(6) $BuNC_{ax}$ 196.9(6)	89.7(3,1.9)[j2]	22
$cis\text{-}Mn^1(CO)_4\{(PPh_2O)_2H\}$	or	$P2_12_12_1$	4	976 1372 1946	 	MnC_4P_2	P 234.9(1,7) OC 182.5(5,6) OC_{ax} 185.6(5,7)	928(5)[k1]	23
$Mn(CO)_4(C_{32}H_{26}NO_2P_2)$[k2]	m	C2/c	8	4020.7(20) 1290.1(5) 1937.9(6)	 118.94(2) 	MnC_4P_2	P 235.6(4,4) OC 181.9(12,26)	84.7(1)[k2]	24
$Mn^1(CO)_4\{SC(NPh)P(S)Ph_2\}$	m	$P2_1/c$	4	1109.5(3) 966(3) 2256.7(3)	 103.11(2) 	MnC_4S_2	S 240(1,10) OC 181(4,3) OC_{ax} 187(4,4)	90.8(2,3.5)[l] 178(2)	25
$cis\text{-}[Mn^1(CO)_2\{P(OMe)_2Ph\}_4].PF_6$	m	P2/c	2	1451(1) 942(1) 1860(2)	 124.5(2) 	MnP_4C_2	P 227.2(4,10) OC 178(13)	90.5(6)[m1]	26
$trans\text{-}[Mn^1(CO)_2\{P(OMe)_2Ph\}_4](PF_6)$	m	$P2_1/n$	4	2299(3) 1438(2) 1421(2)	 107(2) 	MnP_4C_2	P 227.1(7,10) OC 183.9(17)	 177.9(8)[m2]	26
$Mn^1(CO)_4(PPh_3)Cl$	tr	P1	2	9970(4) 1176.5(4) 963.6(4)	924(1) 96.71(1) 73.22(1)	MnC_4PCl	P 239.8(4) Cl 235.8(5) OC 175.2(15)(2x) OC_{ax} 183.9(14,20)	89.4(4,1.8)[n] 177.2(5)	27

Table 2, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn^1(CO)_4\{SC(NPh)PPh_2\}$	tr	P1	2	989.4(9) 1042(8) 1088.5(8)	91.45(4) 97.10(4) 100.53(5)	MnC_4PS	P 231(1) S 238.3(3) OC 181.2(5,4) OC_{ax} 185.2(5,3)	92.6(2,3.3)^{O_1} 171.5(2)	25
$Mn^1(CO)_4\{SC(NPh)PPh_2\}$	tr	P1	2	989.3(6) 1049.7(5) 1093(7)	91.42(3) 972(2) 100.64(4)	MnC_4PS	P 231.6(1) S 239.8(1) OC 181.5(5,5) OC_{ax} 186.2(4,7)	O_2	28
$Mn(CO)_3(PPh_3)(CSNMe_2)$	tr	P1	2	960.5(11) 1100.5(12) 1151.6(12)	77.71(6) 97.83(6) 97.62(7)	MnC_4PS	P 240.4(3) S 234.9(3) OC 180(6,16) LC 192.4(6)	93.3(3,6.3)^{O_3}	29
$[Mn(CO)_3(PPh_3)\{C(SMe)NMe_2\}]BF_4$	m	$P2_1$	2	958.1(12) 1655.9(9) 872.7(15)	101.81(6)	MnC_4PS	P 236.7(5) S 236.3(6) OC 184.9(24,51) LC 184.3(17)	93.1(8,6.1)^{O_4}	29
$Mn^1(CO)_4Br\{PPh_2\text{-}C(O)CH_2CHClCH_3\}$	m	$P2_1/c$	4	1371.2(2) 950.2(2) 1661.1(7)	93.99(2)	MnC_4PBr	P 233.7(3) Br 250(2) OC 185.5(12,25)	91.5(5,2.8)^{P} 173.1(5)	30
$[fac\text{-}Mn_1(CO)_3(NH_3)_3][Mn(CO)_5]$	or	Pnma	4	1245.1 953.4 1227		MnC_3N_3 MnC_5 ^{r_2}	N 290.6(7,1) C 176.9(9,6)	89.3(3,1.9)^{q}	6
$Mn^1(CO)_3(py)_2(F_3CCOO)$	m	$P2_1/c$	4	1261.5(2) 851.2(2) 1594(2)	96.761(9)	MnC_3N_2O	O 204.2(5) N 209.8(7,12) C 178(1,2)	88.6(4,1)$_5$	15
$[Mn^1(CO)_3(NH_2NHCS_2CH_3)]Br$	or	Pbca	8	2193.3(5) 2698(1) 713.4(4)		MnC_3N_2S	S 234.7(7) N 212(2,4) C not given	not given	31

Table 2, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore		M-L [pm]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn^1(CO)_3(PPh_3)_2H$	m	C2/c	4	2354(1) 967.2(3) 1594.1(7)	 114.90(4) 	MnC_3P_2H	H P C	146(8) 226.7(2) 180.5(6,11)	t_1	32
$Mn^1(CO)_3(PPh_2Me)_2H$	m	C2/c	8	1679(1) 1720(1) 1903(1)	 106(1) 	MnC_3P_2H	H P OC	1.5 225.5(-,2) 178	t_2	33
fac-$Mn^1(CO)_3(NCS)(dppm)$	m	$P2_1/n$	4	1804(3) 1285(2) 1223.5(2)	 98.89(2) 	MnC_3P_2N	N P OC OC	201.5(4) 233.9(1,4) 178.7(5) 182.4(5,4)	91.7(2,3)[u]	34
fac-$Mn^1(CO)_3Br\{P(OMe)_2Ph\}_2$	or	$P2_12_12_1$	4	1719(2) 1671(2) 827(1)	 	MnC_3P_2Br	Br P OC	253.2(5) 230(4,4) 186(1,1)	90(5,1.6)[v1]	35
mer-$Mn^1(CO)_3Br\{P(OMe)_2Ph\}_2$[v2]	m	$P2_1/n$	8	1494(2) 2494(3) 1334(1)	 109.6(2) 	MnC_3P_2Br	Br P OC	252.4(7) 227(8,10) 180(3,0)	93.4(12,2.8)[v3] 173.3(10)	35
						$MnC_2P_2Br_2$	Br P OC	253.2(9,2) 225.9(7,1) 187(3,3)	90.6(9,4)[v4] 178.6(18)	
fac-$Mn^1(CO)_3Cl(dmap)$	or	Pbca	8	1527.9(8) 1544.5(8) 1398.2(8)	 	MnC_3As_2Cl	Cl As OC	241.5(9) 243.2(6,0) 174(4,4)	91(2,1)[x]	36
fac-$Mn^1(CO)_3Br\{S_2CCMe_2PPh_3\}$[y]	m	$P2_1/c$	4	981.1(6) 1961.5(7) 1292.2(8)	 90.69(5) 	MnC_3S_2Br	Br S OC	253.6(1) 236.6(1,15) 178(5,17)	91(2,3.5)[y]	37

Table 2, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore		M-L [pm]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn^1(CO)_3Cl\{P(Ph_2)C_5H_7N_2\}$ [V2]	m	$P2_1/c$	8	1416(6) 1616.5(8) 1900.2(6)	 105.67(3) 	MnC_3NPCl	Cl N P OC	237.1(6) 211(1) 233(6) 179(2,3)	91(1,2) [Z1]	38
						MnC_3NPCl	Cl N P OC	237.5(7) 209(1) 230.1(6) 184(2,10)	91.6(9,5.4) [Z2]	
fac-$Mn^1(CO)_3Br\{Ph_2PC(S)NPh_4\}$	m	C2/c	8	2446(8) 1316(3) 1945(6)	 132.68(2) 	MnC_3SPBr	Br S P OC	255.7(2) 238.1(3) 231.5(3) 181.2(12,29)	[Z3]	28
$Mn^1(CO)_2(ac)(PPh_3)_2$	m	$P2_1/c$	4	1774.4(2) 969.2(1) 2000.4(2)	 106.195(4) 	$MnC_2O_2P_2$	P O OC	226.8(3,8) 206.8(7,2) 173.1(13,30)	89.3(5) [Z4]	39
cis-cis-$[Mn^1(CO)_2(phen).$ $.\{P(OMe)_3\}]ClO_4$	tr	P1	2	1332(2) 859.5(1) 1376.4(2)	104.11(2) 114.68(1) 96.48(1)	$MnC_2N_2P_2$	P N OC OC_{ax} P_{ax}	222.2(2) 206.9(5,13) 177.1(8) 181.5(9) 229.3(2)	88.3(3) [Z5]	40
cis-trans-$[Mn^1(CO)_2(phen).$ [Z6] $.\{P(OMe)_3\}]ClO_4$	m	$P2_1/c$	4	1137.70(5) 1346.50(5) 1828.80(5)	 77.504(4) 	$MnC_2N_2P_2$	P N OC	224.7(2,6) 205.6(4,0) 178.5(5,1)	91.8(2) [Z7]	41
	m	$P2_1/m$	4	2272.8(5) 1355.5(2) 900.6(1)	 76.45(1) 	$MnC_2N_2P_2$	P N OC	225.2(2,2) 206(5,2) 179.4(7,3)	90.3(3) [Z8]	

Footnotes, Table 2

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c At 198 K.
d By neutron diffraction.
e C-Mn-H = 82.9(7,1) and 178.8(8)°.
f C-Mn-O = 88.7(2,4.9) and 175.6(2)°.
g C-Mn-Cl = 88.3(2,2) and 179.3(4)°.
h_1 C-Mn-P = 87.6(2,2.4) and 178.2(2)°.
h_2 C-Mn-P = 86.3(2,2.8) and 178.3(2)°.
i_1 OC-Mn-CL = 89.9(4,1.5) and 176.3(4,1.4)°; OC-Mn-Br = 88.8(3,6) and 177.4(3)°; LC-Mn-CL = 89.1(4)°; LC-Mn-Br = 87.9(3,1.6)°.
i_2 OC-Mn-CL = 90(2,5) and 176(2,0)°; OC-Mn-Br = 90(2,2) and 177(2)°; LC-Mn-CL = 93(2)°; LC-Mn-Br = 86(1,2)°.
j_1 OC-Mn-CL = 90.0(3,1.4) and 175.8(2)°; OC-Mn-N = 92.8(2,3.2) and 175.2(2)°; LC-Mn-CL = 86.3(2)°; LC-Mn-N = 92.5(2,3.3) and 174.8(3)°; N-Mn-N = 79.3(2)°.
j_2 OC-Mn-CL = 93.7(2,1.2) and 174.6(2)°; OC-Mn-N = 94.4(2,1.6) and 174.4(2,6)°; LC-Mn-N = 83.1(2.2)° and N-Mn-N = 79.2(2)°.
k_1 The value of P-Mn-P angle.
k_2 At 150 K; the value of P-Mn-P angle; OC-Mn-CO = 90.9(5,3.7) and 178.3(5)°; OC-Mn-P = 90.1(4,2.4) and 174.3(4.1)°.
l C-Mn-S = 89.4(1,6.5) and 177.3(1,1.1)°; S-Mn-S = 901(3)°.
m_1 C-Mn-P = 88.4(3,1.9) and 176.7(5)°; P-Mn-P = 92.1(1,1.9) and 176(2).
m_2 C-Mn-P = 90(6,3.8)°; P-Mn-P = 90.2(3,2.7) and 174.3(3,3)°.
n C-Mn-Cl = 88.8(4,3.9) and 175.3(4)°; C-Mn-P = 93.4(3,3.9) and 172.3(3)°; Cl-Mn-P = 86.55(14)°.
o_1 C-Mn-S = 88.6(2,5.4) and 170.7(2)°; C-Mn-P = 92.2(2,5.5) and 167.0(2)°, S-Mn-P = 730(4)°.
o_2 C-Mn-S = 88.6(2,5.6) and 170.8(2)°; C-Mn-P = 92.2(2,5.7) and 167(2); and S-Mn-P = 72.9(0)°.
o_3 OC-Mn-CL = 87.3(3)°, 106.8(3) and 153.5(3)°; OC-Mn-P = 90.3(2,1.5) and 176.8(2)°; OC-Mn-S = 101.4(2,8.3) and 150.5(2)°; LC-Mn-P = 90.7(2)°; LC-Mn-S = 44(2)°; and S-Mn-P = 87.3(1)°.
o_4 OC-Mn-CL = 88(8), 105.9(7) and 154.9(8)°; OC-Mn-P = 88.7(5,1.8) and 176.1(7)°; OC-Mn-S = 101.9(7,5.2) and 152.9(6)°; LC-Mn-P = 92.2(4)°; LC-Mn-S = 48.3(5)°; and S-Mn-P = 86.3(1)°.
p C-Mn-P = 91.1(4,1.4) and 175.2(4)°; C-Mn-Br = 86.1(4,1.6) and 178.1(4)°; and P-Mn-Br = 90.5(1)°.
q C-Mn-N = 92.5(3,1.7) and 177.8(3,1.2)°; and N-Mn-N = 85.9(2,7)°.
r Data given in Table 1.
s C-Mn-O = 93.9(3,1.7) and 176.7(3)°; C-Mn-N = 92.4(3,3.1) and 177.2(4,4)°; O-Mn-N = 84.7(3,1.1)°; and N-Mn-N = 87.6(3)°.
t_1 H-Mn-C = 79(3) and 180(3)°; P-Mn-C = 92.7(3,2.6)°; and P-Mn-P = 169.66(8)°.
t_2 P-Mn-C = 92 and 93°, and P-Mn-P = 175°.
u C-Mn-N = 90.6(2,7) and 177.4(2)°; C-Mn-P = 95.6(2,3) and 167.2(2,6)°; N-Mn-P = 84.9(1,2.2)°; and P-Mn-P = 71.3(1)°.

Footnotes, Table 2 (continued)

v_1 C-Mn-P = 89.3(4,4) and 175(4,1.8)°; C-Mn-Br = 86.4(4,1) and 175.4(5)°; P-Mn-Br = 92.2(2,2.8)°; and P-Mn-P = 96(1)°.
v_2 There are two crystallographically independent molecules.
v_3 C-Mn-P = 89.9(8,2.3)°; C-Mn-Br = 86.7(8,2.8) and 178.5(7)°; P-Mn-Br = 90.3(2,3.7)°; and P-Mn-P = 178.7(7)°.
v_4 C-Mn-P = 89.9(7,2.4)°; C-Mn-Br = 89.4(9,4.8) and 178.1(6)°; P-Mn-Br = 90.4(3,3.8)°; and P-Mn-P = 179.1(11)°.
x C-Mn-Cl = 92(1,2) and 177(1)°; C-Mn-As = 92(1,2); Cl-Mn-As = 85.7(2,2)°; and As-Mn-As = 87.1(2)°.
y At 163 K; C-Mn-S = 93.5(2,4.8)°; C-Mn-Br = 90.5(2,3.8) and 176.8(2)°; S-Mn-Br = 90(1,2.6)°; and S-Mn-S = 72.5(1)°.
z_1 C-Mn-Cl = 88.8(7,1.7) and 180(7)°; C-Mn-N = 98.1(8,5.6) and 167.1(9)°; C-Mn-P = 94.5(8,6.4) and 170.2(7)°; Cl-Mn-N = 87.5(4)°; Cl-Mn-P = 91.9(2)°; and N-Mn-P = 66.5(5)°.
z_2 C-Mn-Cl = 89(7,1.9) and 175.1(7)°; C-Mn-N = 94.8(7,2.1) and 166.3(9)°; C-Mn-P = 95(8,3.9) and 164.3(6)°; Cl-Mn-N = 87.9(4)°; Cl-Mn-P = 93.7(2)°; and N-Mn-P = 67.5(5)°.
z_3 C-Mn-S = 94.1(4,1.5) and 171.4(5)°; C-Mn-P = 95.7(4,4.5) and 167.7(4)°; P-Mn-Br = 89.3(1)°; P-Mn-S = 72.5(1)°; and S-Mn-Br = 86.3(1)

z_4 C-Mn-O = 104.6(4,2.1) and 165.9(5,2.2)°; C-Mn-P = 90.8(3,2.3)°; O-Mn-O = 61.6(3)°; O-Mn-P = 879.1(2,4.1)°; and P-Mn-P = 177.4(1)°.
z_5 C-Mn-N = 92.3(3,3.5) and 171.5(3)°; C-Mn-P = 88.3(2,2) and 176.9(2)°; N-Mn-N = 79(2)°; N-Mn-P = 92(2,6.5) and 174.2(2)°; P-Mn-P = 95.28(7)°.
z_6 Two kinds of crystals.
z_7 C-Mn-N = 94.4(2,1) and 173.6(2,2)°; C-Mn-P = 90.2(2,1.7)°; N.Mn-N = 79.5(2)°; N-Mn-P = 89.7(1,1.4)°; and P-Mn-P = 178.63(5)°.
z_8 C-Mn-N = 95.2(3,6) and 174.2(3,7)°, C-Mn-P = 90.4(2,1.1); N-Mn-N = 79.5(2)°; N-Mn-P = 89.6(1,2.1)°; and P-Mn-P = 178.94(7)°.

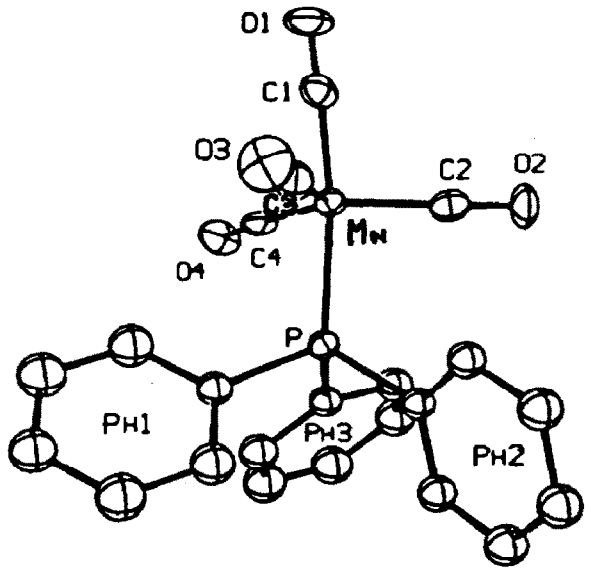

Figure 1. Structure of the $[Mn(CO)_4PPh_3]^-$ Ion.
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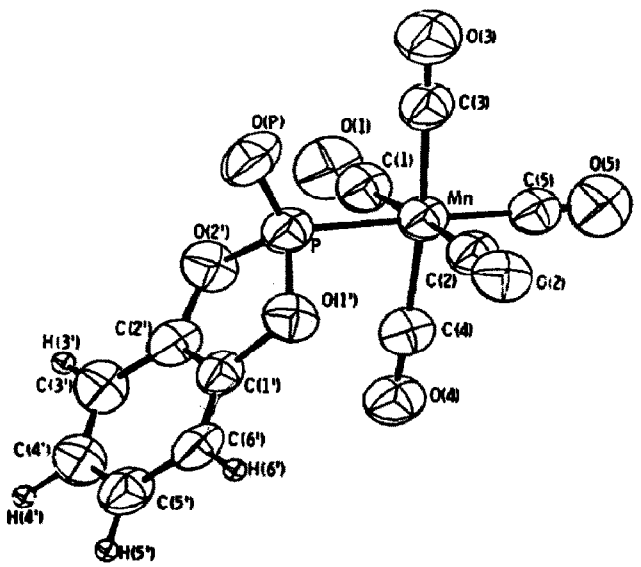

Figure 2. Structure of $Mn(CO)_5\{OC_6H_4OP(O)\}$
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Table 3 Crystallographic and Structural Data for Mononuclear Manganese Carbonyl Compounds with H-borate Ligands[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ¥[°]	Chromophore		M-L [pm]	OC-Mn-CO OC-Mn-H M-Mn-H	Ref
$Mn^1(CO)_3(B_3H_8)$[c]	m	$P2_1/c$	4	1606.9(9)		MnC_3H_3	C[b]	181.5(6,7)	91.1(2,1.2)	42
				590.1(3)	95.10(4)		H	169.3(46,57)	88.3(16,4.9),175.3(16,2.0)	
				1172.2(6)			(B	229.0(7,26)	92.5(22,3.4)	
$Mn^1(CO)_4(B_3H_7Br)$[d]	or	Pmcn	4	765.8(3)		MnC_4H_2	C	184.2(8,25)	91.2(4,1.3),177.6(4)	43
				908.4(3)			H	177.7(2x)	88.4(0,3.5;177.7(0)	
				1542.6(5)			(B	235.6(9,0))	93.8(0)	
$Mn^1(CO)_3(B_9H_{13})$	or	Pmcn	4	1154.9(2)		MnC_3H_3	C	181.5(3,2)	92.5(2,2)	44
				550.6(1)			H	167.6(35)	87.6(9,3.2),177(11,9)	
				1926.0(3)			H	180.7(28)	94(15,4.9)	
							(B	225.7(4,26))		
$(PPh_3Me)[Mn^1(CO)_3(B_9C_2H_8)]$	tr	P1	2	1121.6(5)	105.79(1)	MnC_5	OC	177.2(4,8)	not given	45
				1128.5(4)	104.46(1)		C	204.5(4,2)		
				1146.4(5)	98.04(1)		(B	222.7(5))		
							(B	235.3(5,4))		
$Mn(CO)_3(B_9H_{12})(thf)$	tr	P1	2	982.8(3)	90.1(2)	MnC_3H_2	C	180.2(5,12)	91.43(20,2.97)	46
				1330.5(5)	104.23(2)		H	170(-,8)	91.39(-,4.7),173.91(-,38)	
				693.7(2)	109.87(3)		(B	222.1(4,15)	not given	
$Mn(CO)_3(B_9H_{12})(Et_3N(CH_2)_4O)$	tr	P1	2	1001.8(2)	99.61(15)	MnC_3H_2	C	178.6(7,13)	92.3(3,1.6)	47
				1284.3(3)	94.545(14)		H	167(-,3)	not given	
				930.5(2)	96.918(15)		(B	222.9(7,33))	not given	
$Mn(CO)_3\{B_9H_{12}(OC_4H_8)\}$	tr	P1	2	1286.6(23)	90.21(6)	MnC_3H_2	C	179.3(5)	90.61(20.53)	48
				979.2(21)	108.12(6)		H	175(4)	91.32(-,1.46),175.7)(-,1.48)	
				718.3(13)	104.48(6)		(B	221.7)6,21)	93.45(-,2.20)	

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c At 178K.
d At 173(2)K.

The effects of steric hindrance of the ligands can be seen in the elongation of Mn-P bonds for PR_3 compounds. Thus the mean values for Mn-P are: 225.2 pm ($P(OMe)_3$) <227.6 pm ($P(OMe)_2Ph$)<231.0 pm (PPh_3). Another factor affecting bond lengths is the coordination number of the manganese, the former increasing as the latter increases from four to five to six. For example the mean Mn-CO distances are: 174.8 pm (four coordinate) <179.4 pm (five coordinate) <181.6 pm (six coordinate). The mean Mn-PPh_3 distances are 226.8 pm (five coordinate) <231.0 pm (six coordinate).

3. Compounds with H-borate ligands

The data for this class of compounds are listed in Table 3. The crystal structure of yellow $Mn(CO)_4(B_7H_7Br)$ [43] is shown in Figure 3, in which six coordination is achieved by four carbonyls (Mn-C = 184.2(8.25)pm) and a bidentate B_3H_7Br ligand via two Mn-H-B bridge hydrogen bonds (Mn-H = 177.7 pm).

The mean Mn-CO bond distance of 180.4 (range 176.5 to 186.7 pm) as well as Mn-HL bond distances of 173.7 (range 164 to 183 pm) are shorter than those found for mononuclear manganese carbonyls at 181.6 and 174.2 respectively (Table 2). The mean Mn-HL bond distance elongates in the order: 169.3 pm (HL = H_8B_8) <174.2 pm ($H_{13}B_8$) <175 pm ($H_{12}B_8$) <177.7 pm H_2B_8Br). This reflects the steric hindrance associated with each of the ligands.

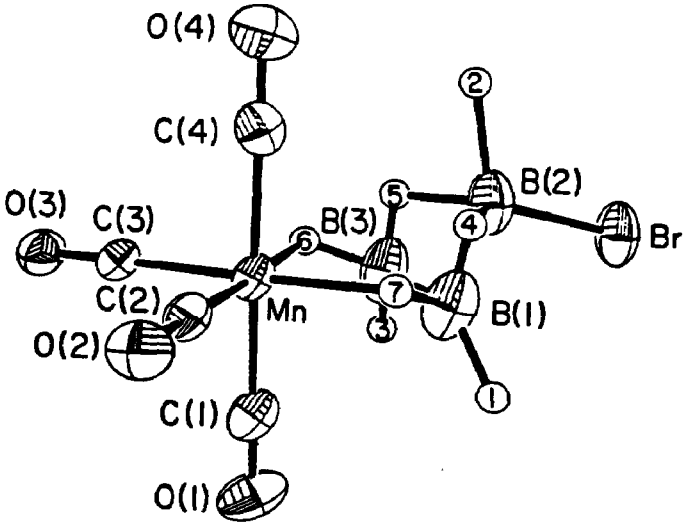

Figure 3. Structure of $Mn(CO)_4(B_3H_7Br)$
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(B) Binuclear Carbonyl Compounds

Crystallographic and structural data for the binuclear derivatives are summarized in Table 4. The structures are tabulated in the order of increasing distance between the manganese atoms. There are several distinct types of bridging, the distorted edge-shared bi-octahedral structure with two bridging ligands being the most common. In two cases, $Mn_2(CO)_8(\mu\text{-}Cl)_2(thf)_2$ [73] and $Mn_2(CO)_8(\mu\text{-}Cl)_2$ [73a], two chlorine atoms function as bridges. Two bromine atoms serve this role in $Mn_2(CO)_8(\mu\text{-}Br)_2(P_2Ph_4)$ [75] and $Mn_2(CO)_8(\mu\text{-}Br)_2$ [78]. In several cases two sulphur ligands serve as the bridges, as in $Mn_2(CO)_8(\mu\text{-}pmte)_2$ [31] and four other hexacarbonyldimanganese derivatives [51, 69, 79, 82]. In two cases [70, 71] nitrogen ligands link tetracarbonylmanganese moieties. Two PX_2 ligands bridge the $Mn(CO)_4$ units in two other examples [76, 77].

In another two examples, [50, 64], two MnC_4HP octahedra are bridged by hydrido and PPh_2 ligands. The last type of bridge involves phosphorus and carbon ligands in $Mn_2(CO)_7(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)$ [50]. In this series of binuclear compounds the Mn-Mn distance is smaller than 300 pm only if the value of the Mn-L-Mn bridge angle is less than 92°.

The crystal structure of dark red $Mn_2(CO)_7(N{=}C(CF_3)_2)_2$ [49] is shown in Figure 4. Both nitrogen atoms of the hexafluoroisopropylidenimine ligands and a carbonyl carbon atom bring the manganese atoms within 251.83(24)pm with the

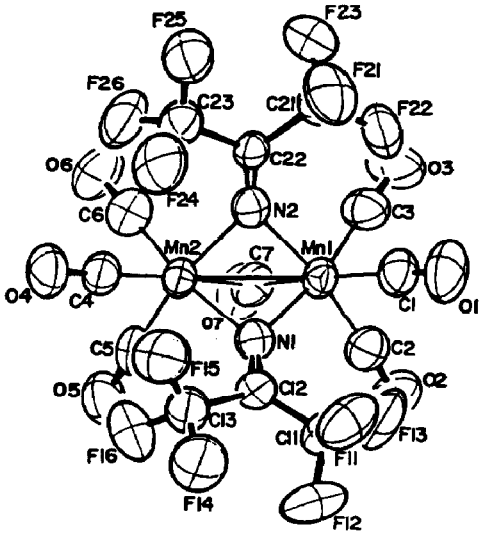

Figure 4. Structure of $Mn_2(CO)_7(N{=}C(CF_3)_2)_2$
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Table 4 Structural Data for Binuclear Manganese Carbonyl Compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn_2(\mu\text{-}CO)\{\mu\text{-}N{=}C(CF_3)_2\}_2(CO)_6$	m	$P2_1/c$	4	929.8(5) 2661.4(19) 954.3(8)	1210.0(5)	MnC_4N_2	OC[b] 182.0(10,49) OC[b] 205.9(9,115) N[c] 200.2(7,35)	251.83(24) C[b] 75.19(34) N 77.71(26,14)	89.87(39,2.57) d	49
$Mn_2(\mu\text{-}CH{=}CH_2)\mu\text{-}PPh_2(CO)_7$[e]	tr	P1	4	1030.1(4) 1032.0(4) 2435.9(11)	92.70(3) 92.17(3)	MnC_5P	OC 184.3(4,11) C 226.4(4) C[c] 207.2(5,15) P[c] 231.1(2,58)	273.8(2) C 83.10(2) P 73.00(1)	90.7(2,4.6) 176.7(2) e	50
						MnC_5P	OC 183.9(6,16) C 226.4(7) C[c] 207.8(6,25) P[c] 231.1(1,54)	275.0(2) C 82.40(3) P 72.6(1)	90.6(2,5.8) 173.8(3) e_1	
$Ph_2[\eta_2\text{-}C(\mu_2\text{-}S){=}C(\mu_2\text{-}S)]Mn_2(CO)_6$	m	$P2_1/a$	4	1812.4(3) 1006.4(3) 1196.5(3)	90 107.47(4) 90	MnC_3S_2	OC 180.6(9,25) S[c] 223.1(2,7)	277.4(2) S 74.30(1,1)	91.4(4,1.5) f_1	51
						MnC_5S_2	OC 181.9(9,8) C 220.0(6,17) S[c] 236.3(2,3)		89.8(4,1.9) f_2	
$[(OC)_3Mn^1(\mu\text{-}N_3)_3Mn^1(CO)_3](NEt_4)$	m	$P2_1/n$	4	1030 1021 2192	91.1	MnC_3N_3	OC 175(2,7) N[c] 208(2,3)	289.3(4) N 88.6	not given	52
$Mn^0_2(CO)_{10}$[g]	m	I2/a		1408.8(3) 685.0(2) 1424.2(3)	105.08(1)	MnC_5	OC 185.6(2,9) OC_{ax} 181.5(2)	289.50(6) -	91.85(9,4.65)	53
$Mn^0_2(CO)_{10}$	m	I2/a	4	1413.50(19) 709.99(9) 1462.77(22)	105.167(15)	MnC_5	OC 185.6(2,9) OC_{ax} 181.1(3)	290.38(6) -	91.72(11,3.78) 172.57(10,190)	53a
$Mn^0_2(CO)_{10}$	m	I2/a	4	1416(2) 711(2) 1467(2)	105.0(5)	MnC_5	OC 183.1(16.24) OC_{ax} 179.2(14)	292.3(3) -	91.8(6,4.3) 172.3(6,2.2)	54

Table 4, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L	[pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn^0_2(CO)_8(PMe_2Ph)$	m	C2/c	8	2365.6(5) 1312.3(5) 1371.5(5)	 99.89(5) 	MnC_5	OC	176	290.4 -	not given	55
						MnC_4P	OC P	176 223.9			
$Mn^0_2(CO)_8(PMePh_2)_2$	m	$P2_1/c$	4	1539 849 2615	 95.7 	MnC_4P	OC P	175 223	290 -	not given	56
$Mn^0_2(CO)_8\{P(OMe)_3\}_2$	or	Fdd2	8	3877.8 1791.6(2) 695.5(1)		MnC_4P	OC P	184.0(21,77) 216.9(5)	291.2(3) -	89.8(9,8.0) 170.2(9,3.5) h_1	57
$Mn^0_2(CO)_8(PEt_3)_2$						MnC_4P			290.32(14)	 h_2	58
$Mn^0_2(CO)_8(PEt_3)_2$	or	Aba2	8	1594(3) 1478(3) 1160(2)		MnC_4P	OC P	181(4,7) 224.7(7)	291.3(6) -	not given	59
$Mn^0_2(CO)_7(bdmp)$	m	C_{cc}	4	1731.2(3) 815.6(2) 1726.1(3)	 124.28(2) 	MnC_4P	OC P	181.7(7,31) 225.3(1)	292.0(1) -	92.05(5,6.7) 176.2(6) h_3	60
						MnC_7P	OC C P	180.3(8,7) 217.2(6,28) 257.3		91.5(4,5.6)	
$Mn^0_2(CO)_5(mdpp)_2$ $.CH_2Cl_2.C_6H_{14}$	m	Cc	4	1965.0(3) 1690.8(2) 2225.3(4)	 130.89(1) 	MnC_3P_2	OC_c OC^c P	168(3,2) 193(3) 225.7(9,22)	293.4(3) C 96(1)	180.2 i_1	61
						MnC_4P_2O	OC_c OC^c CO P	171(34) 201(3) 229(2) 228.8(9,24)		98(1) i_2	

Table 4, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn_2(CO)_4(\mu\text{-}pCH_3C_6H_4NC)$. .$(mdpp)_2$	tr	P1	2	1465.19(19) 1484.07(20) 1752.87(2)	69.881(10) 83.360(11) 60.286(8)	MnC_3P_2N	OC 178(1,1) C^c 214(1) N 212(1) P 226.9(3,10)	293.6(2) C 95.9(5)	99.0(5) j_1	62
						MnC_3P_2	OC 179(1,2) C^c 181(1) P 224.6(3,1)		102.1(5) j_2	
$Mn_2(CO)_4(\mu\text{-}H)(\mu\text{-}Br)$(tedip)	or	Pbca	8	3306.6(22) 1443.5(7) 1480.6(7)		$MnC_2P_2HB_2$	OC not given H^c not given Br^c 248.1(4,4) P 221.2(5,4)	293.6(3) Br 72.6(1) H not given	k	63
$Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}PPh_2)$	m	I2/c	4	1676(2) 815(7) 1703(2)	110.46(2)	MnC_4HP	OC 181.4(18,36) H^c 186(6) P^c 228.4(6)	293.7(5) H 104.1(4.8) P 80.04(27)	90.57(80,5.94) 177.23(74) l	64
$Mn^o_2(CO)_8(AsMe_2Ph)_2$	m	C2/c	4	1075 1394 1849	98.15	MnC_4As	OC 178 As 246	294 -	not given	56
$Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}PPh_2)$. .$(CNBu)_2$	tr	P1	2	1768.6(3) 1006.3(2) 923.1(3)	96.92(4) 99.40(4) 104.34(5)	MnC_4HP	OC 180.5(6,25) C 194.2(4,10) H^c 165(-,2) P^c 228.2(2,2)	295.9(1) H 127 P 80.8(1)	91.8(2,5.9) m	50
$Mn^o_2(CO)_8(mdpa)_2$	tr	P1	2	1119.1(1) 1649.8(5) 945.5(1)	93.64(2) 109.08(2) 89.36(2)	MnC_4As	OC 178(2,6) As 240.9(2,2)	296.2(3)	91.7(8,5.3) 171.8(8,4) n_1	65
$Mn^o_2(CO)_8(f_4fars)$	or	$Pna2_1$	4	1747.9(3) 1027.3(3) 1271.3(3)		MnC_4As	OC 180(2,3) As 239.9(2,7)	297.1(2) -	92.6(4,3.7) 168.8(4,6) n_2	376 377
$Mn_2(CO)_8I_2(f_4fars)$	m	$P2_1/c$	4	1385(2) 1479(1) 1396(2)	102.2(1)					377

Table 4, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn^0_2(CO)_{10}$						MnC_5	OC 180.3(16) OC 187.3(5)	297.7(11)	93.4(5)	68
$Mn_2(CO)_8\{\mu\text{-}SC(SMe)(NMe)\}_2$	m	$P2_1/n$	4	984.5(2) 1379.1(4) 1497.2(5)	98.23(4)	MnC_3S_2N	OC 180.6(4,11) S[c] 242.7(1,14) N 202.9(3,6)	323.3(1) S 95.12(4,5)	90.3(2,3.5) p	69
$[PhH{=}NMn(CO)_4]_2$	tr	$\bar{P}1$	1	723.6(1) 888.9(2) 946.8(2)	80.52(2) 77.38(1) 77.44(1)	MnC_4N_2	OC 185.17(26,157) N[c] 202.71(16,43)	323.49(8) N 105.87(8)	89.87(10,1.96) 177.83(10) q	70
$Mn_2(CO)_8(\mu\text{-}NSOF_2)_2$	m	$P2_1/n$	2	1002.4(5) 1175.7(5) 736.8(4)	100.96(4)	MnC_4N_2	OC 180.7 OC_{ax} 189.9 N[c] 211.2(6,4)	331.8(2) N 103.5	not given	71
$Mn_2(CO)_4(\mu\text{-}Br)_2(tedip)_2$	or	Pbca	4	1537.8(4) 1632.7(5) 1445.3(4)		$MnC_2P_2Br_2$	OC not given P 224.0(6,2) Br[c] 252.4(4,2)	351.7(4) Br 88.4(1)	r	63
$Mn_2(CO)_8(\mu\text{-}Br)(B_3H_8)$	m	$P2_1/c$	4	1092.1(8) 705.2(4) 1898.2(12)	113.05(6)	MnC_3H_2Br	OC 180(10,30) H 161.8(-,141) Br[c] 250.7(3,2)	355(0) Br 90.02(9)	90.04(45,18) s	72
$Mn_2(CO)_8(\mu\text{-}Cl)_2(thf)_2$	m	$P2_1/c$	2	852.4(1) 1091.2(2) 1133.8(1)	112.80(1)	MnC_3Cl_2O	OC 178.9(7,10) O 210.0(4) Cl[c] 239.7(2,2)	356(2) Cl 95.9(1)	89.3(3,5) t	73
$Mn'_2(CO)_8(\mu\text{-}pmte)_2$	tr	$\bar{P}1$	1	1096.0(3) 1037.3(2) 1107.6(3)	130.65(8) 129.50(7) 85.20(7)	MnC_3S_2N	OC 181(2,1) N not given S[c] 238.0(6,32)	356.3(4) 596.9(2)	89.1(8,1.1) u	31
$Mn'_2(CO)_8(\mu\text{-}Cl)_2$	m	$P2_1/c$	4	942.1(2) 1158.9(2) 1276.7(1)	109.68(2)	MnC_4Cl_2	OC 185.2(3,46) Cl[c] 239.5(1,1)	356.9(1) Cl 96.3(1,0)	90.5(1,5) 178.5(1,1) v	74

Table 4, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$Mn'_2(CO)_8(\mu\text{-}Br)_2(P_2Ph_4)$	tr	P1	2	1087.4(8) 1184.1(9) 1244.4(9)	96.59(4) 100.55(5) 95.37(4)	MnC_3Br_2P	OC not given P[c] not given Br[c] 252.6(5)	366.1(2) Br 92.5(5)	not given	75
$Mn'_2(CO)_8(\mu\text{-}PMe_2)_2$	or	Pbca	4	1345.4(3) 1262.1(3) 1125.2(5)		MnC_4P_2	OC 183(1,2) P[c] 234.7(3,2)	367.5(2) P 103.1(1)	92.9(6,5.8) 175.7(6) x_1	76
$Mn'_2(CO)_8(\mu\text{-}PH_2)_2$	tr	P1	1	680.4(3) 706.4(5) 919.1(6)	110.50(5) 91.92(5) 115.65(4)	MnC_4P_2	OC 183.6(4,13) P[c] 235.1(1,1)	370.3(3) P 103.9(1)	92.5(2,2.0) 174.0(1) x_2	77
$Mn'_2(CO)_8(\mu\text{-}Br)_2$	m	$P2_1/c$	4	957(1) 1179(2) 1291(2)	109.30(1)	MnC_4Br_2	OC 181(5,12) Br[c] 252.6(10,12)	374.3(8) Br 95.6(4,1)	91.2(2.0,3.2) 175.2(1.9,7) y	78
$Mn_2(CO)_8(mbt)_2$	m	C2/c (C2)		1438(2) 1184(2) 1390(2)	94.70(8)	MnC_3S_2N	-	-	-	79
$Mn_2(CO)_9(CNPh)$	m	$P2_1/c$	4	1232 917 1788	108.3	MnC_6	-	-	-	20
$Mn_2(CO)_8(\mu\text{-}As)(Me_2AsCCF_3)_2$	tr	P1	2	958.0(4) 1527.9(6) 929.2(3)	93.07(2) 119.26(2) 82.80(2)	MnC_3As_3 MnC_6As	-	-	-	80
$(OC)_4Mn\{\mu\text{-}P(S)Me\}Mn(CO)_5$	m	$P2_1/n$	4	659.4(3) 1520.6(3) 1631.2(3)	93.29(3)	MnC_5P	OC not given P[c] 239.4(2)	P 129.4(1)	-	81
						MnC_4SP	OC not given S 241.4(2) P[c] 228.9(2)	-	z_1	

Table 4, cont. (6)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	M-M[pm] M-L-M[°]	OC-M-CO cis-[°] trans-[°]	Ref
$[PhCH_2NEt_3]_2[Mn(CO)_3.(\mu\text{-}S_3CS)]_2$	tr	$P\bar{1}$	2	9128(9) 9720(12) 1330.8(6)	71.91(7) 79.97(6) 69.86(9)	MnC_3S_3	OC not given S_c 236.0(4) S^c 237.3(4,8)	S 97.80(14)	z_2	82
$(OC)_4Mn(\mu\text{-}AsMe_2)_3.Mn(CO)_3Cl$	m	$P2_1/c$	4	1414.2(3) 1043.1(3) 1495.7(2)	90.28(1)	MnC_4As_2	OC 179-189 As_c 239.6(4) As^c 250.2(4)	As 123.6(1)	88.2-94.9(9) z_3	83
						MnC_3As_2Cl	OC 179-189 Cl 237.1(7) As_c 238.6(4) As^c 246.2(4)		88.2-94.9(9) z_4	
$[(OC)_4MnPPh_2O]_2$	m	$P2_1/c$	4	1158(2) 1680(3) 1920(3)	116.39(5)	MnC_4OP	OC 183.4(19,53) O 204.9(8,10) P 235.8(5,5)	-	90.9(7,3.0) 176.1(7,1.0) z_5	84
$(OC)_5Mn(\mu\text{-}SCOCOS)Mn(CO)_5$	m	$P2_1/n$	2	662.2(2) 1079.0(7) 1262.4(9)	94.93(5)	MnC_5S	OC 184.1(2) OC 187.6(1) S 237.9(1)	-	92.6(1)	85
$(OC)_5Mn\{\mu\text{-}SC(C_6H_4F\text{-}4)_2CS\}.Mn(CO)_5$	m	$P2_1/n$	2	1072.2(3) 1175.7(2) 1123.6(3)	90 111.16(3) 90	MnC_5S	OC 185.5(8,53) S 240.5(2)	-	90.9(3,3.6) 173.5(3,2.9) z_6	51 86
$\{[(CCO_2C_6H_{11})_2(OC)_4MnS]_2.(\mu\text{-}CS(C_6H_4F\text{-}4)_2CS)\}$	tr	$P\bar{1}$	1	1112.4(2) 1131.6(3) 1227.4(3)	88.48(2) 66.69(2) 80.31(2)	MnC_5S	OC 182.9(8,37) C 200.9(6) S 243.4(2)		90.8(3,4.6) 173.2(3) z_7	51 86
$Mn_2(CO)_6\{P_2(t\text{-}BuN)_2.P_2(t\text{-}BuN)_2\}$	m	$P2_1'n$	4	1023.1(3) 1493.7(4) 1126.0(2)	106.42(2)	MnC_4P_2	OC 183.6(5,14) P 229.3(1) P 250.7(1)	-	not given	87

Footnotes, Table 4

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom (ligand)
d OC-Mn-C^c = 83.02(37,1.64) and 168.05(38,1.68)°; OC-Mn-N^c = 97.39(34,6.45) and 168.56(34,1.65)°; C^c-Mn-N^c = 89.41(31,2.93)°; N^c-Mn-N^c = 76.81(25,98)°.
e There are two crystallographically independent molecules; OC-M-CL_c = 82.0(2), 97.3(2) and 172.5(2)°; OC-Mn-C^c = 84.1(2) - 175.2(2)°; OC-Mn-P^c = 94.1(2,9.3) and 167.0(2,3.8)°; C-Mn-C^c = 36.5(2)°; C^c-Mn-P^c = 87.5(2,1.2)°; P^c-Mn-C = 85.7(2)°.
e_1 OC-Mn-CL = 82.6(2), 97.8(2) and 170.7(2)°, OC-Mn-C^c = 82.6(2) - 173.9(2)°; OC-Mn-P^c = 94.8(2,9.9) and 166.8(2,7.1)°; C-Mn-C^c = 36.3(2)°; C^c-Mn-P^c = 86.9(2,9)°; P^c-Mn-C = 84.6(2)°.
f_1 OC-Mn-S^c = 96.5(3,9.4) and 164.6(3,3.0)°; S^c-Mn-S^c = 86.6(1)°.
f_2 OC-Mn-S = 98.7(4,7.5) and 165.9(3,3.5)°; S^a-Mn-S^a = 80.7(1)°.
g At 74K.
h_1 OC-Mn-P = 93.5(6,3.9)°.
h_2 not given
h_3 OC-Mn-P = 88.8(3,2), 105.0(3) and 156.3(3)°.
i_1 P-Mn-P = 177.0(3)°; OC-Mn-CO^c = 126(1,6)°.
i_2 P-Mn-P = 174.9(4); OC-Mn-CO^c = 131(1,5)°; OC-Mn-OC = 99(1) and 163(1)°; OC-Mn-OC^c = 29(1)°
j_1 OC-Mn-C^c = 130.5(4,8.7)°; OC-Mn-N = 105.1(4) and 155.9(4)°; OC-Mn-P = 89.8(3,1.9)°; P-Mn-C^c = 90.6(3,4)°; P-Mn-N = 89.4(3,1.4)°; P-Mn-C^c = 90.6(3,4)°; P-Mn-N = 89.4(3,1.4)°; P-Mn-P = 175.9(1)°; N-Mn-C^c = 34.1(4)°.
j_2 OC-Mn-C^c = 112.8(5) and 145.1(5)°; OC-Mn-P = 88.0(3,1.1)°; P-Mn-C^c = 93.2(3,9)°; P-Mn-P = 173.5(1)°.
k P-Mn-P = 177.5(2,1.4)°.
l OC-Mn-P = 93.04(59,3.61) and 166.81(62)°; OC-Mn-H = 86.76(57,7.86) and 175.2(2.4)°; H-Mn-P = 87.9(2.4)°.
m OC-Mn-CL = 88.9(2,2.2) and 176.8(3,9)°; OC-Mn-H^c = 90(-,7) and 171(-,2)°; OC-Mn-P = 95.4(2,3.7) and 165.1(2,1.9)°; LC-Mn-H^c = 93(-,6)°; LC-Mn-P = 89.4(2,4)°; and P-Mn-H^c = 76(-,1)°.
n_1 OC-Mn-As = 91.1(6,4.1) and 174.0(6,2.7)°.
n_2 OC-Mn-As = 89.1(4,1.3) and 178.4(4,5)°.
o Gaseous state, by electron diffraction.
p OC-Mn-S^c = 93.3(2,7.6) and 170.4(1,4.5)°; OC-Mn-N = 95.9(2,4.5) and 168.6(2,1)°; N-Mn-S^c = 68.4(1,1) and 92.4(1,3)°; S^c-Mn-S^c = 84.12(4,9)°.
q OC-Mn-N = 92.85(8,10.59) and 171.43(8,5.72)°; N-Mn-N = 74.13(8)°.
r P-Mn-P = 167.6(2)°.
s OC-Mn-Br^c = 90.80(28,76) and 178.33(25,23)°; OC-Mn-H = 91.49(-,12.05) and 175.21(-,1.67)°; H-Mn-Br^c = 84.82(-,9.76)°; and H-Mn-H = 89.72(-,5.86)°.

Footnotes, Table 4 (continued)

t OC-Mn-O = 93.9(3,2) and 175.2(2)°; OC-Mn-Cl = 91.3(2,2.0) and 177.6(2,2)°; O-Mn-Cl = 88.7(1,5.1) and Cl-Mn-Cl = 84.1(1)°.
u S-Mn-S = 83.1(2).
v OC-Mn-Cl = 90.6(1,2.6) and 176.5(1,4)°, and Cl-Mn-Cl = 83.7(1,1)°.
x_1 OC-Mn-P = 89.6(4,3.5) and 169.1(4,9)°; and P-Mn-P = 76.9(1)°.
x_2 OC-Mn-P = 90.0(1,5.2) and 170.8(1,5)°; and P-Mn-P = 76.1(1)°.
y OC-Mn-Br = 89.9(1.4,3.9) and 176.4(1.5,9); and Br-Mn-Br = 84.4(3,4)°.
z_1 S-Mn-P = 51.1(1)°.
z_2 S^C-Mn-S^C = 82.20(14)°, and S^C-Mn-S = 87.53(13)°.
z_3 As-Mn-As =91.7(1)°; OC-Mn-As = 86.1 - 93.8(8)°.
z_4 As-Mn-As = 90.8(1)°; OC-Mn-As = 85.3(2,8)°.
z_5 OC-Mn-O = 88.8(5,8.1) and 174.2(6,2)°; OC-Mn-P = 90.4(6,2.9) and 177.7(5,2)°; and P-Mn-O = 88.1(3,2)°.
z_6 OC-Mn-S = 86.7(2,4.7) and 177.2(2)°.
z_7 OC-Mn-S = 88.1(2,20.3) and 161.3(2)°.

Mn-N-Mn and Mn-C-Mn angles of 77.71(26.14)° and 75.19(34)° respectively. This is the shortest Mn-Mn distance found in manganese carbonyl compounds, being even shorter than that found for the coordination compounds of manganese [383] of 271.6 pm. There is an example of bridging via the α-N atoms of the three azide groups in $[Mn_2(CO)_8(\mu\text{-}N_3)_3.NEt_4$ [52]. The Mn-Mn distance of 289.3(4) pm as well as the Mn-N-Mn bridge angle of 88.6° are larger than those found in the previous example [49], again showing the elongation of the Mn-Mn distance as the Mn-L-Mn angle opens.

There are several cases in which two MnC_5 or $MnC_4P(As)$ moieties are held together through a direct metal-metal bond: $Mn_2(CO)_{10}$ [53, 53a, 54]; $Mn_2(CO)_9$-(PMe_2Ph) [55]; $Mn_2(CO)_8L_2$, L=$PMePh_2$ or $AsMe_2Ph$ [56], $P(OMe)_3$ [57], PEt_3 [58, 59] and bdmp [60]. The mean Mn-Mn bond distance of 290.6 pm for MnC_5 chromophores is about 0.9 pm shorter than those for MnC_4P (As), reflecting the steric effect of the larger P or As donor ligands.

There are two examples in which two manganese atoms are joined by a single bond, 293.4(6) pm [61] and 293.6(2) pm [62]. In the former there are also two trans-diphosphine ligands and a carbonyl as bridges. In the latter, the carbonyl bridge is replaced by an isocyanide. The carbonyl bridge [61] is tridentate and donates a pair of electrons to one manganese (Mn-C = 193(3) pm) and a second pair of electrons to the other (Mn-C = 212(1)pm, Mn-O = 214(1)pm). The isocyanide bridge (62) is also tridentate, donating a pair of electrons to one manganese (Mn-C = 181(1)pm) and a second pair of electrons to the other (Mn-N = 212(1)pm, Mn-C = 214(1)pm).

In another two examples, $Mn_2(\mu\text{-}H)$ $(\mu\text{-}Br)(CO)_4$ $(tedip)_2$ and $Mn_2(\mu\text{-}Br)_2$ $(CO)_4(tedip)_2$ [63], in spite of the fact that they are structurally analogous, only the former case has a single Mn-Mn bond (293.6(3)pm). In the latter the distance of 351.7(4) pm indicates non-bonding between the two metal atoms. In both cases the two manganese atoms are bridged by two trans tetraethyldiphosphite ligands and two bridging ligands, hydrogen and bromine in the former, two bromine atoms in the latter. The elongation of the Mn-Mn distance observed above reflects steric hindrance in the latter case, with simultaneous increase in the value of the Mn-L-Mn bridge angle from 72.6(1)° to 88.4(1)°, respectively.

A single bond between two manganese (0) atoms has been found for $Mn_2(CO)_8(mdpa)_2$ (296.2(3)pm) [65] and $Mn_2(CO)_8(fyfars)$ (297.1(2)pm) [66, 67]. The molecular structure of both compounds can be considered to be derived from the parent $Mn_2(CO)_{10}$ molecule by the replacement of one equatorial CO ligand on each manganese atom with one of the arsenic atoms of the mdpa or fyfars ligand which then serves to bridge the manganese(O) atoms.

In the remaining examples (Table 4) there is no other case with a direct metal-metal bond, these involving one, two, three or four bridging atoms. The data show that the oxidation states of the manganese are zero and one, with the

latter more common. The number of examples representing the various crystal classes increases in the order: orthorhombic <<triclinic <<monoclinic.

There is an example, $Mn_2(\mu\text{-}CH{=}CH_2)$ (μPPh_2) $(CO)_7$ [50] in which two crystallographically independent molecules differ by degree of distortion, being the only example in this series of distortion isomerism. Non-equivalent manganese atoms are found in a number of cases. These are: five and seven coordinate [51, 61]; five and eight coordinate [60]; five and six coordinate [62]; six and seven coordinate [80]. There are examples with differing chromophore: MnC_5 and MnC_4P [55]; MnC_5P and MnC_4SP [81]; MnC_4As_2 and MnC_3As_2Cl [83]. In the remaining cases (Table 4) the manganese pairs have the same chromophore.

The influence of temperature on the degree of distortion has been reported for $Mn_2(CO)_{10}$ [53]. Both electronic as well as steric factors influence the Mn-L bond distance, which increases in the order: 234.7 pm (PMe_2) <239.1 pm ($AsMe_2$); 223.9 pm (PMe_2Ph) <246.0 pm ($AsMe_2Ph$); 226.5 pm (P_2-mdpp) <240.4 pm (As_2-mdpa).

The mean Mn-L(terminal) bond distance increases in the order: 181.0 pm (CO) <205.6 pm (NL) <212.5 pm (CL) <232.0 pm (PL) <237.1 pm (Cl) <240.8 pm (AsL). For the Mn-L(bridge) distance the increase is in the order 172 pm (H) <200.0 pm (CO) <204.4 pm (NL) <207.0 pm (CL) <229.4 pm (PL) <232.9 pm (SL) <239.6 pm (Cl) <248.2 pm (AsL) <251.0 pm (Br). In general these trends follow the van der Waals radii of the coordinating atom.

It is noted that the mean bridge distance is longer than the terminal distance when L is CO (200.0 vs 181.9 pm), Cl (239.6) vs 237.1 pm), or As(L) (248.2 vs 240.8). The opposite is true when L is N(L) (204.4 vs 205.6 pm, C(L) 207.0 vs 212.5 pm, or F(L) (229.4 vs 232.0 pm).

(c) Tri-, Tetra- and Hexanuclear Carbonyl Compounds

The structural data for these compounds are given in Table 5. There are eight trinuclear examples which can be organized into five distinct bridging types. A scalene triangle of manganese atoms is observed for $Mn_3(CO)_8(PMe_2Ph)(\mu_3\text{-}OEt)_2$ [88,89] and $Mn_3(CO)_9(\mu\text{-}OEt)_2(\mu_2\text{-}F/I)$ [89], with two face bridging ethoxy groups and one edge bridging ethoxy in the former, and halogen in the latter. The dimensions of the manganese triangle remains remarkably constant in all three compounds. The mean Mn-Mn distance increases with increasing size of the edge bridging group in the order: 286.5pm(F) <287.2 pm(OEt) <289.6 pm(I).

The crystal structure of another type is shown in Figure 5. The metal carbonyl system in $[Mn(CO)_4]_3(\mu\text{-}N_2Me)$ [90] consists of a bent Mn-Mn-Mn skeleton with typical metal-metal single bond distances (280.7(4) and 282.6(3)pm). The terminal diazo N(1) forms a bridge between Mn(2) and Mn(3) which causes the central manganese atom Mn(2) to have the unusual coordination number seven with the MnC_4NMn_2 chromophore.

Table 5 Structural data for tri-, tetra- and hexanuclear manganese carbonyl compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M [pm]	M-M-M M-L-M [°]	Ref
$[Mn_3(CO)_8(\mu\text{-}OEt)_3(PMe_2Ph)$	m	$P2_1/b$	4	1760.9(2)		MnC_3O_2	OC[b] 175(2,5)	253.8(4)	60.0(1,12.7)	88
				2131.9(3)			O[c] 201(1,1)	286.7(2)	90.0(6,14.3)	89
				922.0(2)	127.16(1)			321.4(3)	d_1	
						MnC_3O_3	OC 177(2,6)		d_2	
							O[c] 206(1,3)			
						MnC_2O_3P	OC 178(2,1)		d_3	
							O[c] 202(1,6)			
							P 229.0(5)			
$[Mn_3(CO)_8(\mu_3\text{-}OEt)_2(\mu_2\text{-}F)]$	m	$P2_1/b$	4	934(1)		MnC_3O_2	OC[c] 176(4,24)	260.2(8)	60.0(2,11.1)	89
				1988(2)			O[c] 197(2,2)	282.9(7)	93(1,13)	
				1023(1)	89.65(6)			316.5(7)	e_1	
						$MnC_3O_2F(2x)$	OC[c] 176(4,30)		e_2	
							O[c] 199(2,5)			
							F[c] 195(2,2)			
$[Mn_3(CO)_8(\mu_3\text{-}OEt)_2(\mu_2\text{-}I)]$	m	$P2_1/b$	4	967(1)		MnC_3O_2	OC[c] 173(4,3)	270.5(8)	60.0(2,9.2)	89
				1870(1)			O[c] 210(2,1)	283.5(8)	90.0(1,11.0)	
				1126(1)	86.25(5)			314.8(7)		
						$MnC_3O_2I(2x)$	OC[c] 177(4,8)		f_1 f_2	
							O[c] 204(2,6)			
							I[c] 279.1(6,102)			
$\{[Mn(CO)_4]_3(\mu_3\text{-}N_2Me)\}$[g]	m	C4	4	989.1(2)		MnC_4N	OC[c] not given	280.7(4)	107.4(7)	90
				1460.7(3)	96.23(5)		N[c] 196.8(8,93)	282.6(3)	93.8(4)	
				1319.6(5)						
$(Ph_4As)[Mn_3(CO)_{14}]$[h]	tr	P1	2	1161.4(11)	100.89(5)	$MnC_5(2x)$	OC 180.6(37,55)	288.3(4)	180.0(0)	90
				964.6(12)	96.66(6)				h_1	
				1802.2(22)	90.96(5)					
						MnC_4	OC 179.5(36,24)		h_2	
						MnC_5	OC 182.0(38,91)	290.6(5)	180.0(0)	
									h_3	
						MnC_4	OC 179.8(36,5)		h_4	

Table 5, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore		M-L [pm]	M-M [pm]	M-M-M M-L-M [°]	Ref
$Mn_3(CO)_{11}(dmp)$	m	$P2_1/n$	4	855.6(2) 1850.3(3) 1329.2(2)	 92.67(1) 	$MnC_4P(2x)$	OC P	181.3(9,28) 227.8(2,89)	291.7(1) 305.3(1)	99.8(1) 79.0(1,7),157.5(1) i_1	60
						MnC_7P	OC LC P	180.9(10,17) 218.5(8,32) 246.8(2)		i_2	
$Mn_3(CO)_{12}(\mu_2\text{-}H)_3$	tr	P1	2	822(1) 1486(2) 899(1)	105.2(1) 118.5(1) 96.9(1)	MnC_4H_2	OC OC$_{ax}$ H^c	178.9(12,34) 185.4(14,20) 172(12,11)	309.9(2) 310.7(2) 312.6(2)	60.0(1,5) 131(7,18) j	92
$[Mn(CO)_4(\mu_2\text{-}PH_2)]_3$	m	$P2_1/n$	2	905.2(2) 974.8(2) 1264.2(2)	90 109.14(2) 90	MnC_4P_2	OC P^c	183.8(2,21) 238.1(1,7)	430.3(1) 435.6(1)	- 130.0(-,2.6)	77 k
$[Mn_4(CO)_{15}S_4]$	m	$P2_1/c$	4	928.8(5) 1548.4(2) 1816.2(25)	 96.02(8) 	$MnC_3S_3(2x)$	OC S^c	179.4(9,17) 235.0(2,43)		- 114.03(8,17.29) l_1	93
						MnC_4S_2	OC S^c	184.1(9,36) 234.3(3,2)		l_2	
						MnC_5S	OC S^c	187.2(9,37) 238.2(2)		l_3	
$[Mn^I_4(CO)_{12}(\mu_3\text{-}F/OH)_4]$.(C6H6)2	c	Pn3m	2	1127.71(5)		$MnC_3(F/O)_3$	OC F/O^c	180.2(3) 205.2(3)	319.9(1)	- 102.4(1) m	94
$[Mn_6(CO)_8\{\mu\text{-}OP(OEt)_2\}_8]$	m	$P2_1/n$	4	2020.1(7) 1251.2(5) 3478.0(9)	 95.57(3) 	$Mn^{II}O_5(3x)$	O	215(-,14)	388 398	not given	95
						$Mn^IC_3P_3(3x)$	OC P	not given 228(-,3)			

Footnotes for Table 5

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom (ligand).
d_1 C-Mn-C = 88.6(1,1.4)°; C-Mn-O = 102.3(7,5.3)° and O-Mn-O = 70.7(5)°.
d_2 C-Mn-C = 88.8(9,1.9)°; C-Mn-O = 97.9(8,5.7)° and O-Mn-O = 80.8(5,12.8)°.
d_3 C-Mn-C = 83.6(8)°, C-Mn-O = 99.3(7,5.7) and 170.6(8,5.3)°; O-Mn-O = 76.3(5,7.5)°; C-Mn-P = 87.8(9,2.9)°; 97.5(5,5.3); 169.6(3)°.
e_1 C-Mn-C = 89(2,4)°; C-Mn-O = 103(2,5); 161(2,1)°; O-Mn-O = 66(1)°.
e_2 C-Mn-C = 86(2,3)°; C-Mn-O = 103(2,1); 167(2,3)°; O-Mn-O = 65(1,1)°; C-Mn-F = 94(2,4); 179(1,2)°; O-Mn-F = 79(1,1)°; Mn-F-Mn = 93(1)°.
f_1 C-Mn-C = 84(2,7)°; C-Mn-O = 106(2,8); 166(2,3)°; O-Mn-O = 68(1)°.
f_2 C-Mn-C = 90(2,7)°; C-Mn-O = 98(2,4); 168(2,4)°; O-Mn-O = 71(1,2)°; C-Mn-I = 84(1,3); 172(1,3)°; O-Mn-I = 91(1,3)°; Mn-I-Mn = 60.9(2)°.
g At 238K.
h There are two crystallographically independent anions.
h_1 C-Mn-C = 92.9(16,5.3) and 167.0(17,2.2)°.
h_2 C-Mn-C = 88.9(15) and 180.0(00)°.
h_3 C-Mn-C = 92.8(16,5.1) and 167.4(14,4)°.
h_4 C-Mn-C = 90.0(15) and 180.0(0)°.
i_1 C-Mn-C = 90.9(4,9.6) and 177.6(5,6)°, C-Mn-P = 97.9(3,24.5) and 150.6(3,7.5)°.
i_2 C-Mn-C = 89.6(5,4.5)°; C-Mn-P = 110.4(3,1.3) and 153.0(3)°.
j C-Mn-C = 90.7(6,3.7) and 177.2(6,4)°; C-Mn-H = 80(4,7) and 171(4,6)°; H-Mn-H = 108(6,10)°.
k C-Mn-C = 90.9(1,3.7) and 177.9(1,1.6)°; C-Mn-P = 89.5(1,6.0) and 176.7(1,4)°; P-Mn-P = 89.1(1,1.8)°.
l_1 C-Mn-C = 91.2(4,7.9)°; C-Mn-S = 96.9(3,11), 167.8(3,8.7)°; S-Mn-S = 52.82(7,8) and 86.9(8,5.62)°.
l_2 C-Mn-C = 90.9(4,3.0) and 176.4(4)°; C-Mn-S = 89.2(3,3.3) and 177.7(3,1)°; S-Mn-S = 90.08(8)°.
l_3 C-Mn-C = 90.7(4,4.0) and 174.7(4,2.7)°; C-Mn-S = 88.7(3,3.8) and 179.2(3)°.
m O-Mn-O = 76.1(1)°; C-Mn-C = 88.5(1)°; C-Mn-F(O) = 97.5(1)°.

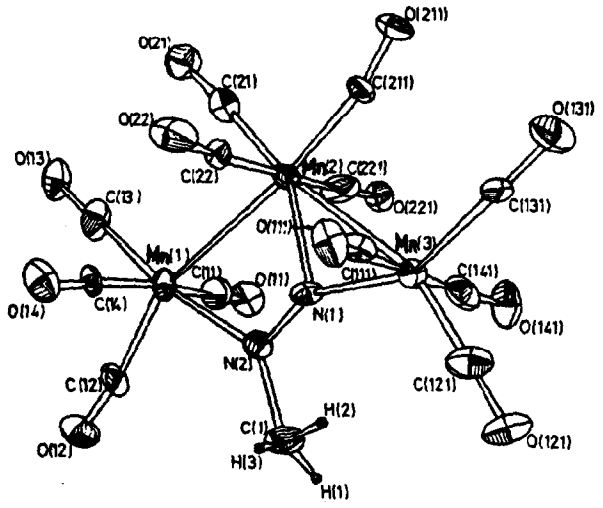

Figure 5. Structure of $[Mn(CO)_4]_3(\mu_3\text{-}N_2Me)$ Reproduced with permission from Angewandte Chemie [90]

An X-ray investigation of red $(Ph_4As)[Mn_3(CO)_{14}]$ [91] shows that the geometry of the $[Mn_3(CO)_{14}]$ anion is essentially D_{4h}, with the three manganese atoms collinear (Mn-Mn-Mn = 180.0(0)°). The central $Mn(CO)_4$ unit is staggered with respect to the other two sets of equatorial CO groups. The Mn-Mn distance of 288.3(4) pm indicates a single bond between the neighbouring manganese atoms. The mean Mn-C bond distance increases with increasing coordination number, 179.5 (MnC_4) versus 180.6pm (MnC_5) (Table 5).

Difference Fourier techniques have been applied to locate the hydrogen atoms in $Mn_3(CO)_{12}(\mu_2\text{-}H)_3$ [92]. The molecular structure of the trimer consists of an equilateral array of manganese atoms, each with four terminal CO groups. The hydrogen atoms lie in the equatorial Mn plane in symmetrically bridging positions. The bond distances and angles are given in Table 5.

The molecule of $[Mn(CO)_4(\mu_2\text{-}PH_2)]_3$ [77] consists of the six membered ring where manganese atoms are bridged by PH_2 groups. The three manganese atoms have the same chromophore, MnC_4P_2.

There are two examples [93,94] of tetranuclear manganese carbonyls. The structure of red $Mn_4(CO)_{13}S_4$ is shown in Figure 6. Two disulphide ligands link the four manganese atoms which each achieve an approximate octahedral

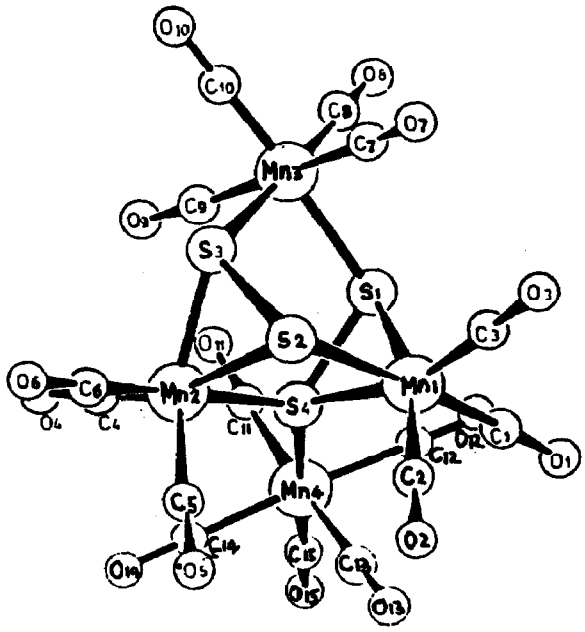

Figure 6. Molecular Structure of $Mn_3(CO)_9\{OP(OEt)_2\}_3$ Reproduced with permission from Z. Naturforsch. [93]

arrangement of ligands. The structure of the other tetranuclear [94] consists of a cubane type of cluster with $Mn(CO)_3$ units at one set of corners and fluoro or hydroxy groups at the other set. With its very high crystallographic symmetry $\bar{4}3m$ it is unique for clusters of this type.

The only example of a hexanuclear, $Mn_6(CO)_9$ $[OP(OEt)_2]_3$ [95], is shown in Figure 7. There are two different types of manganese atoms, the interior three Mn(II) atoms each coordinate in approximately trigonal planar fashion MnO_5, and three exterior Mn(I) atoms each bond to three phosphorus atoms and three carbonyl groups MnC_3P_3 (Table 5).

It is apparent from the data in Table 5 that the mean Mn-L distance increases with coordination number. For example, the mean Mn-P distance is: 227.8 pm (five coordinate) <229.0 pm (six coordinate) <246.8 pm (seven coordinate). The mean Mn-L(bridge) distance increases with increasing van der Waals radius of the ligand atom: 172pm(H) <195 pm(F) <202.3 pm(OEt) <238.1 pm(PH_2) <279.1 pm(I). Interestingly, the mean Mn-CO distance of 180.1 pm is about 0.9 pm smaller than that of the binuclears at 181.0 pm (Table 4).

There are two crystallographically independent $[Mn_3(CO)_{14}]^-$ anions which

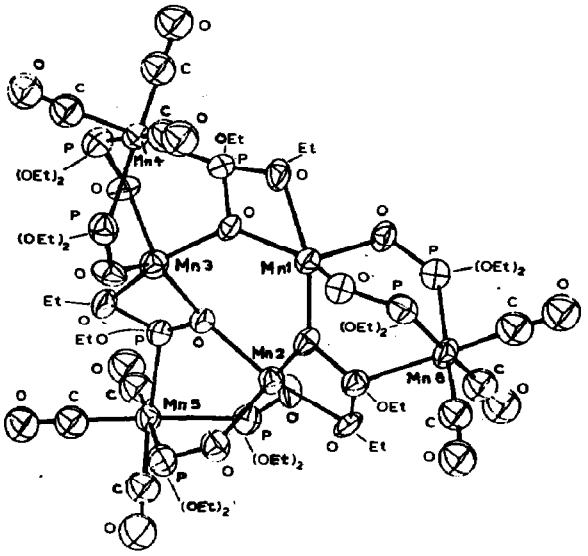

Figure 7. Molecular Structure of $Mn_6(CO)_8\{OP(OEt)_2\}_8$ Reproduced with permission from J. Organomet. Chem. [95]

differ mostly in degree of distortion [91], representing an example of distortion isomerism.

(D) Heteronuclear Carbonyl Compounds

1. Hetero-binuclear derivatives

Structural data for these derivatives are summarized in Table 6. There are six distinct types of bridging, a distorted octahedral manganese singly bonded to another hetero-central atom being the most common [96-101,108]. The mean Mn-M distance increases with the covalent radius of M: 240.7 pm (Si, 118 pm) <243.2 pm (Ge, 122 pm) <255.7 pm (Hg, 138.6 pm) <258.9 pm (Sn, 140 pm). The mean Mn-CO distance follows the same trend (Table 6).

The molecular geometry of red $Mn(CO)_3$ (dmp)PdBr [102] consists of a bimetallic MnPd unit spanned by two bridging mutually trans dmp ligands, bringing the two metal atoms to within 281.0(2) pm.

Molecular structures of yellow α- and orange ß-$Mn(CO)_3Br$(triphos)$Cr(CO)_3$ [103] are shown in Figure 8. The overall geometry of both isomers consist of two metal atoms (Mn and Cr) linked together by the triphos ligand. The coordination

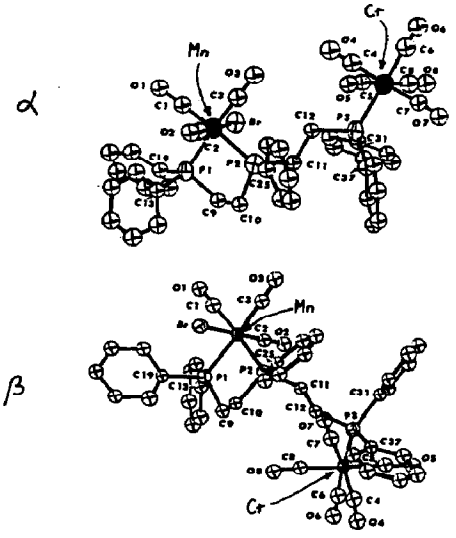

Figure 8. Molecular Structure of α- and ß- $Mn(CO)_3Br(triphos)Cr(CO)_5$ Reproduced with permission from Inorg. Chem. [103]

around the manganese(1) atom in both structures is essentially octahedral (MnC_3P_2Br) with three carbonyl groups cis to each other.

The essentially octahedral environments around manganese(I) atoms in the two isomers differ mostly by degree of distortion, another example of distortion isomerism.

The fourth type of bridging involves one ligand atom, for example phosphorus in $Mn(CO)_4(PPh_2)_2Fe(CO)_4$ [104], arsenic in $Mn(CO)_4(PPh_3)(AsMe_2)Fe(CO)_4$ [105], and oxygen in $Mn(CO)_5(OTeF_5)$ [109]. The arsonium derivative [105] exists in two isomeric forms which differ in the cis-trans arrangement of the P and As atoms on manganese, leading to different degrees of distortion.

The fifth type is found in $(Mn(CO)_4(AsMe_2)_2Fe(CO)_4]^+[Mn(CO)_4Cl)(AsMe_2)$-$Fe(CO)_4]^-$ [106], where two bimetallic MnFe units are bridged by two $AsMe_2$ ligands in the cation and only one $AsMe_2$ ligand in the anion.

A sixth type of bridging involves three atoms, for example in $Mn(CO)_3(\mu$-$H)(\mu,\mu,$-dtal)$Fe(CO)_3$ [107] the bridging involves two nitrogen atoms of dtal and a hydrogen atom. The Mn-Fe distance of 253.93(9) pm is much shorter than that found in $Mn(CO)_4(PPh_2)Fe(CO)_4$ [104] which is 282.5(5) pm.

Table 7 Structural data for hetero-trinuclear manganese carbonyl compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] [°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L' [°]	Ref
(tpy)Cd{Mn(CO)$_5$}$_2$	m	$P2_1/c$	4	915.8(15) 1889.5(26) 1696.0(17)	 111.38(9)	$MnC_5Cd(2x)$	OC[b] 179.5(21,46) Cd[d] 278.0(5,20)	93.4(9,13.6) 82.9(7,6.7),176.1(7,1.9) 132.4(2)[c]	110
(bpy)Cd{Mn(CO)$_5$}$_2$	m	$P2_1/n$	4	1442.9(15) 1580.5(16) 1042.3(10)	 94.62(2)	$MnC_5Cd(2x)$	OC 178.2(15,42) Cd[d] 268.3(3,3)	93.4(7,8.2),164.4(7,7.2) 82.3(5,4.9),177.0(5,5) 127.7(2)[c]	111
(phen)Cd{Mn(CO)$_5$}$_2$	m	$P2_1/n$	4	1457.4(15) 1625.8(16) 1045.3(10)	 96.87(2)	$MnC_5Cd(2x)$	OC[d] 177.5(21,46) Cd[d] 268.1(4,6)	93.5(9,9.3),164.1(9,8.8) 82.2(7,6.1),177.5(7,2.1) 131.4(2)[c]	111
(diglyme)Cd{Mn(CO)$_5$}$_2$	m	$P2_1/n$	4	1016.1(10 2301.0(20) 971.8(9)	 91.80(2)	$MnC_5Cd(2x)$	OC[d] 178.8(11,33) Cd[d] 271.1(2,4)	92.9(5,7.2)167.0(5,7.8) 83.6(4,4.1),176.3(4,1.2) 135.9(1)[c]	112
Hg{Mn(CO)$_5$}$_2$	tr	P1	1	632.5(2) 947.9(2) 633.0(2)	90.86(2) 81.66(2) 97.44(2)	$MnC_5Hg(2x)$	OC 185.4(15,14) Hg[c] 260.8(2)	89.5(7,9) 84.7(5,7),178.9(5) 180[c]	113
Hg{Mn(CO)$_5$}$_2$	tr	P1	1	632.96(11) 948.37(15) 633.32(11)	94.478(6) 81.668(6) 90.816(6)	$MnC_5Hg(2x)$	OC[d] 184.1(16,31) Hg[d] 261.0(2)	92.6(7,3.9),168.7(7,1.1) 84.3(5,8),179.3(5) 180.0[c]	114
(μ-GeMe$_2$)(μ-CO){Mn(CO)$_4$}$_2$[e]	m	C2/c	8	874.2(2) 1421.5(4) 2722.1(7)	 95.05(2)	$MnC_5Ge(2x)$	OC[d] 182.8(9,41) OC[d] 209.6(8,59) Ge[d] 245.5(2,23)	90.7(4,6.3),177.2(4,1) - 71.13(5)[c]	115
$PtMn_2(\mu_2\text{-}PPh_2)_2(CO)_9$	tr	P1	2	1024.0(5) 1081.2(4) 1748.3(8)	94.89(3) 101.41(5) 112.14(3)	$MnC_4PPt(2x)$	OC[d] 182.0(11,33) P[d] 223.9(3,2) Pt[d] 274.4(1,3)	91.90(43,7.36),175.15.47,1.33) not given 159.54(6)[c]	116, 117

Table 7, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L' [°]	Ref
$PtMn_2H(\mu_2\text{-}PPh_2)_3(CO)_8$	tr	P1	2	1094.1(2) 1974.0(5) 1072.0(2)	96.13(2) 105.08(2) 105.22	MnC_4PPt	OC[a] 184.5(18,18) P[a] 230.6(4) Pt 284.7(2)	91.36(71,5.18),179.61(84) f 157.26(6)[c]	117
						MnC_4P_2	OC[a] 182.8(16,21) P[a] 236.7(4,12)	91.93(72,4.24),174.76(71) 90.56(42,6.14),170.40(42,2.54) g	
$(py)_2Pt\{Mn(CO)_5\}_2$							data unavailable		118
$HRe_2Mn(CO)_{14}$	m	$P2_1/n$	4	931(1) 1582(2) 1438(2)	106.25(5)	MnC_5Re	OC 182(3,6) Re 296.0(3)	92.2(1.4,4.5),170.5(1.4,1.1) 85.3(1.0,2.6),178.0(9)	119
$(OC)_8CoFe(\mu\text{-}CO).$ 120 $.(\mu\text{-}Pbu)Mn(CO)_3$	m	$P2_1$	2	859.6(2) 1451.8(2) 875.5(1)	111.01(1)	MnC_4PFe	OC 177-187(1) OC[c] 199(1) P[c] 216.4(5) Fe 269.5(7)	not given h	

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The value of Mn-M-Mn angle.
d The bridge atom (ligand).
e Mn-Mn = 285.4(2)pm, and Mn-C-Mn = 85.8(2)°, Mn-Ge-Mn = 71.1(0)°.
f C-Mn-Pt = 85.00(39) 164.30(47)° and P-Mn-Pt = 51.04(6)°.
g P-Mn-P = 76.63(15)°.
h Co-Mn-Fe = 59.5(1)°.

2. Hetero-trinuclear derivatives

The data for these derivatives are listed in Table 7, and there are three distinct types depending on the metal atoms involved. Most examples involve two manganese atoms with one heteroatom which most commonly serves as a bridge between them [110-114]. The Mn-M-Mn bridge angles are 132.4(4)° [110], 127.2(2)° and 131.4(2)° [111], 135.9(1)° [112] and 180° [113,114]. The mean Mn-Gd distance of 271.4 pm is about 10.5 pm greater than Mn-Hg (260.9 pm) which is consistent with the "lanthanide contraction". The mean Mn-C bond length elongates with the opening of the Mn-M-Mn angle, for example 178.5 pm and 132° for M = Ge [110-112], and 184.3 pm and 180° [113,114] for M = Hg.

Red-orange $[Mn(CO)_4]_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)_2$ [115] contains each manganese atom in approximately octahedral environment sharing an edge defined by the germanium (Mn-Ge = 245.5(2,23) pm and bridging carbonyl (Mn-C = 245.5(2,23) pm. The Mn-Mn bond distance of 285.4(2) pm is the shortest in the heterotrinuclear series, and indicates a single metal-metal bond. The mean Mn-CO(bridge) distance of 209.6 pm is about 26.8 longer than the Mn-CO(terminal) value, as expected.

In another red-orange derivative, $PtMn_2(\mu_2(\mu_2\text{-}PPh_2)_2(CO)_8$ shown in Figure 9, each manganese atom is bonded to four terminal carbonyls (Mn-C = 182.0(11,33)pm), to the platinum atom (Mn-Pt = 274.4(1,3)pm), and to a P atom (Mn-P = 223.9(3,2)pm. The Mn-Pt-Mn bridge angle is 159.56(4)° [117].

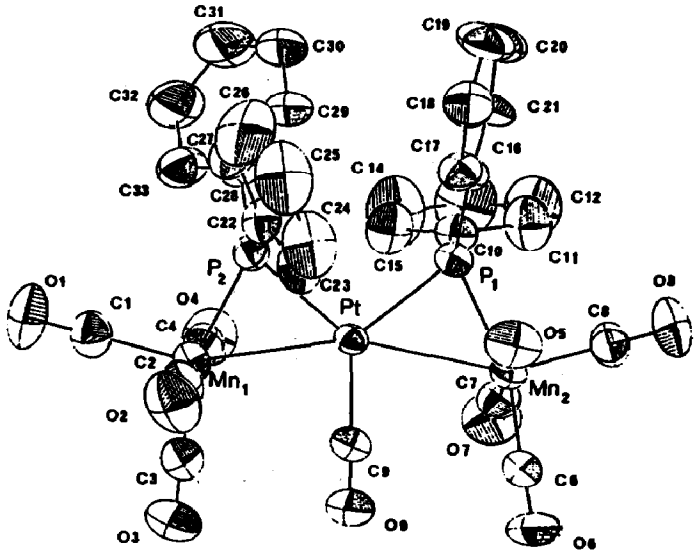

Figure 9. Structure of $PtMn_2(\mu_2\text{-}PPh_2)_2(CO)_8$
Reproduced with permission from J. Organomet. Chem. [117]

The three metal atoms in $HRe_2Mn(CO)_{14}$ [119] are arranged in a cis configuration, the angle at the central rhenium atom Re..Re-Mn being 98.09(7)°. The Mn-Re distance of 296.0(3) pm indicates a single bond.

Examination of the data in Table 7 shows the Mn-CO(terminal) bond distances in the range 174.0 to 188.0 pm with a mean value of 181.6 pm. The Mn-CO(bridge) distances are larger, 199.0 to 215.4 pm (mean 206.0 pm). The mean Mn-CO(terminal) distance of 181.6 pm found for the hetero-trinuclear compounds is shorter than those found in hetero-binuclear compounds (183.1 pm). The Mn-Mn bond distances for both types of derivative are comparable.

3. Hetero-polynuclear compounds

The crystallographic and structural data for these compounds are given in Table 8. There are few examples of hetero-tetranuclear derivatives [121-130], the structure of red $ClSn[Mn(CO)_4(PPh_3)]_3$ [122] being shown in Figure 10 as a representative example. In this case the "central" atom is in fact the tin, and the three $Mn(CO)_4(PPh_3)$ groups plus the chlorine atom occupy the corners of a distorted tetrahedron around it with a mean Mn-Sn bond distance of 271.3(1,8) pm. A similar structure has been found in related $SnMn_3$ derivatives [121, 123, 124]. It is noted that as the PPh_3 ligands replace the stronger π-acceptor CO [122, 123] on the manganese trans to the tin, the Mn-Sn bond length is shortened compared to those derivatives with no phosphine ligands [121, 124].

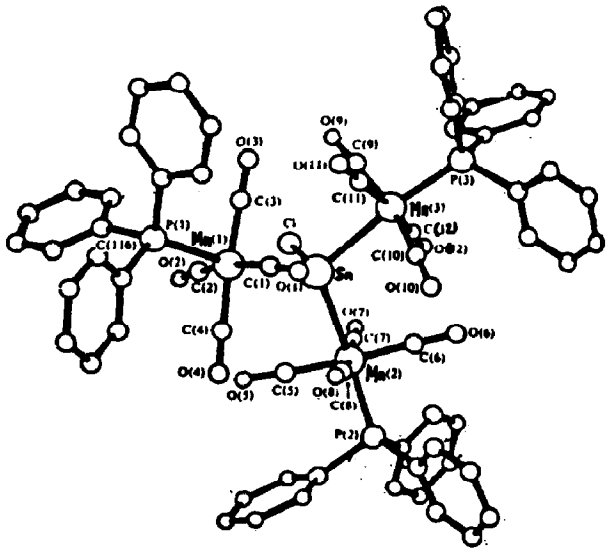

Figure 10. Structure of $ClSn\{Mn(CO)_4(PPh_3)\}_3$
Reproduced with permission from Acta Crystallogr. [122]

Table 8 Structural data for hetero-polynuclear manganese carbonyl compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L [°] Mn-M-Mn	Ref
$BrSn\{Mn(CO)_5\}_3$	m	$P2_1/c$	4	1196.3(5) 1310.6(5) 1490.4(5)	 90.73(5) 	$MnC_5Sn(3x)$	OC[b] 184.1(11,32) Sn[c] 274.0(2,18)	91.61(48,5.75) 86.75(34,7.43),173.64(36,3.27) 116.41(5,2.25)	121
$ClSn\{Mn(CO)_4(PPh_3)\}_3$	tr	P1	2	1341.3(3) 2276.8(4) 1091.6(3)	85.91(10) 89.76(10) 107.74(10)	$MnC_4PSn(3x)$	OC 181.0(7,26) P 229.0(2,14) Sn[c] 271.3(1,8)	89.8(3,6.6),171.0(3,3.5) 86.3(2,7.3) d 116.39(5,2.22)	122
$BrSn\{Mn(CO)_4(PPh_3)\}_3$	tr	P1	2	1351.5(3) 2270.9(4) 1100.4(3)	86.15(10) 90.05(10) 108.33(10)	$MnC_4PSn(3x)$	OC 181.9(7,23) P 228.6(2,12) Sn[c] 271.8(1,10)	89.7(3,7.0),170.9(3,3.5) 86.3(3,6.6) e 116.26(3,2.17)	123
$ClSn\{Mn(CO)_5\}3$[f]	m	Pa	4	1795 908 1502	 107.55 	$MnC_5Sn(3x)$ $MnC_5Sn(3x)$	OC 181(1) Sn[c] 274.0(6,20) OC 181(1) Sn[c] 273.5(6,32)	not given not given 116.5	124
$Fe_2Mn(CO)_8(\mu_3\text{-}5)(\mu_4\text{-}5)\cdot Mn(CO)_5$	m	$P2_1/n$	4	912.5(1) 1340.2(3) 1871.6(4)	90.00(1) 91.672(1) 90.039(2)	MnC_5S MnC_3S_2Fe	OC 179-185 μ_3-S[c] 238.4(3) OC 176-185 μ_4-S[c] not given Fe[c] 271.4(3)	not given 175.3(5) -	125
$[Rh_2(tm4\text{-}br)_4Mn_2(CO)_{10}]\cdot(PF_6)_2(Me_2CO)_2$		Pna2	4	1826.5(11) 2318.5(7) 1783.6(4)	 	$MnC_5Rh(2x)$	OC 277(4,19) Rh[c] 289.4(5,11)	not given 86(1,3),177(2,1) -	126
$Pd_2Mn_2(CO)_6(dppm)_2$	m	$P2_1/c$	4	1756.1(7) 2131.9(8) 1946.1(8)	 113.50(2) 	MnC_5Pd MnC_4PPd_2	OC 180(2,6) Pd[c] 282.1(2) OC 183(2,3) OC[c] 193(2,1) P 229.2(3) Pd[c] 263.9(1,59)	not given not given 99.5(1) g	127

Table 8, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L [°] Mn-M-Mn	Ref
$(OC)_8Mn_2(\mu_2\text{-}PPh_2)_4Pt_2$	m	$P2_1/c$	4	2410.6(8) 1200.2(4) 2084.1(7)	 93.39(2) 	MnC_4PPt	OC 186(1,6) P[c] 224.2(4,1) Pt[c] 271.4(2,4)	91.6(6,6.6),178.5(6)	117
$Mn_2(CO)_8(\mu\text{-}SiPh_2)_2$[h]	m	A2/m	2	1178.8(15) 1048.0(19) 1374.4(22)	 117.37(6) 	MnC_4Si_2	OC 182.9(5,24) Si[c] 240.2(2)	91.6(3,4.8),177.7(3) h 73.39(6)	128
$Mn'_2(CO)_8(\mu\text{-}Br)_2(Se_2Ph_2)$	m	C2/c	4	1161.8(3) 1057.6(3) 1945.6(4)	 106.94(2) 	MnC_3Br_2Se	OC 181(2,1) Se 247.8(3) Br[c] 254.1(3,1)	90.7(9,7) 91.5(7,2.9),176.6(7,1.2) i 92.8(1)	129
$Mn'_2(CO)_8Br_2(Te_2Ph_2)$	or	Pbca		2238.8(8) 913.1(4) 2304.4(8)					129
$[(tpp)SnMn(CO)_4.HgMn(CO)_5]$ $.(CH_2Cl_2)_{0.5}$	tr	- P1	2	1478.5(35) 1487.0(30) 1349.4(22)	92.26(21) 111.33(16) 109.34(26)	MnC_5Hg MnC_4SnHg	OC not given Hg[c] 265.9(11) OC not given Sn 255.4(7) Hg[c] 257.9(11)		130
$Mn(CO)_5Si(SiMe_3)_3$	tr	- P1	2	900.2(2) 965.5(2) 1563.9(3)	83.66(1) 105.65(1) 114.61(1)	MnC_5Si	OC 182(2,3) Si[c] 256.4(6)	91.3(1,5.3),174.0(2,8) 87.4(6,4.1),175.3(7) -	131
$[\{Mn(CO)_5\}_2In(\mu\text{-}Cl)]_2$	tr	- P1	1	1062.2(3) 1039.3(3) 872.2(3)	87.56(2) 95.59(2) 124.58(2)	MnC_5In	OC 184.3(7,23) In[c] 266.5(1,6)	91.91(31,6.69) 85.96(22,6.78),175.80(24,1.24) 123.59(3)	132
$[\{Mn(CO)_5\}_2In(\mu\text{-}Br)]_2$	tr	- P1	1	1063.4(4) 1039.6(8) 882.3(1)	87.79(2) 95.33(1) 124.32(1)	MnC_5In	OC 184.0(7,21) In[c] 266.4(1,6)	91.99(32,6.50) 85.75(22,6.15),175.83(23,75) 124.97(3)	132

Table 8, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L [°] Mn-M-Mn	Ref
$\{Mn(CO)_5\}_2In(\mu\text{-}I)I_2$	tr	$P\bar{1}$	1	1064.9(2) 1045.7(2) 907.3(1)	87.67(1) 95.07(1) 123.79(1)	MnC_5In	OC 183.8(8,21) In[c] 267.2(1,6)	92.00(38,6.32) 85.75(26,5.05),175.56(29,6) 126.37(4)	132
$Mn_2(CO)_8\{\mu\text{-}Ge(Br)Mn(CO)_5\}_2$[j]	m	$P2_1/c$	2	876.2(4) 1212.4(4) 1542.5(4)	 62.89(9)	MnC_5Ge	OC 186.1(11,25) Ge[c] 250.2(2)	90.8(5,2.9) 88.5(4,3.7) 131.12(7,76)	133
						MnC_4Ge_2	OC 183.4(10,34) Ge[c] 248.1(2,1)	90.1(4,5.1),177.7(4) 86.5(3,8.7),173.3(3,1.2) 75.20(5)	
$Mn_2(CO)_8\{\mu\text{-}Ge(I)Mn(CO)_5\}_2$[k]	m	$P2_1/c$	2	898.7(2) 1219.0(3) 1565.9(3)	 61.4(1)	MnC_5Ge	OC 186.5(11,21) Ge[c] 251.9(2)	90.8(5,3.0),176.5(5,4) 88.3(4,2.9),178.1(4) 130.7(1,8)	134
						MnC_4Ge_2	OC 183.5(11,25) Ge[c] 249.6(2,2)	90.6(5,5.2),177.8(5) 86.4(3,9.1),173.8(3,9) 72.0(0)	
$Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2$[l]	tg	$I4_1/a$	8	1350(2) - 2826(3)		MnC_5Ga	OC 184.4(5,12) Ga[c] 244.5(1)	91.97(20,4.23) 85.83(15,3.29) 141.29(2,2)	135
						MnC_4Ga_2	OC 181.7(5,16) Ga[c] 245.5(1,6)	92.19(20,3.31 86.56(14,5.47) 78.86(2)	
$Mn_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2$[m]	tg	$I4_1/a$	8	1372(2) - 2854(3)		MnC_5In	OC 184.4(5,16) In[c] 259.6(1)	92.13(23,4.01) 85.42(16,2.53) 141.27(2,20)	135
						MnC_43In_2	OC 182.5(5,24) In[c] 261.0(1,0)	92.85(23,3.00) 85.93(17,6.02) 76.36(2)	
$H_2Sn_2\{Mn(CO)_5\}_4$	m	C2/c	4	1571(5) 1718(5) 1251(5)	 107.3(2)	MnC_5Sn	OC 182(4,9) Sn[c] 270.3(5,28)	92.1(16,3.7),171.0(16,4.7) 85.5(11,7.2),174.7(10,4) 119.8(1)	136

Table 8, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L [°] Mn-M-Mn	Ref
$Mn_2(CO)_8\{\mu\text{-}Sn(Cl)Mn(CO)_5\}_2$[n]	m	$P2_1/c$	2	873.3(2) 1230.0(2) 1546.4(2)	 115.98(10) 	MnC_5Sn	OC 185.1(5,30) Sn[c] 262.6(1)	91.29(21,2.84) 87.31(14,2.68),176.86(16) 132.75(2)	121
						MnC_4Sn_4	OC 182.9(5,29) Sn[c] 262.4(1,4)	91.30(19,3.42) 85.99(14,8.81),173.10(14,1.87) 72.17(2)	
$Mn_2(CO)_8\{\mu\text{-}Sn(Br)Mn(CO)_5\}_2$[o]	m	$P2_1/n$	2	881.7 1237.6 1551.1	 63.54 	MnC_5Sn	OC 185.4(6,21) Sn[c] 263.4(1)	91.27(26,2.37) 87.35(18,3.06) 132.22(3)	137
						MnC_4Sn_4	OC 183.2(6,25) Sn[c] 262.8(1,3)	91.23(24,3.50) 86.00(17,8.57),173.00(18,1.49) 71.91(2)	
$Br_2Sn_2\{Mn(CO)_5\}_4$	m	$P2_1/c$	4	1659.1(5) 1245.5(2) 1721.4(8)	 108.10(3) 	MnC_5Sn	OC 184.2(9,17) Sn[c] 272.7(1,23)	91.3(4,4.2),174.2(4,1.0) 87.3(3,4.1),177.3(3,2.4) 119.17(4,50)	138
$Fe_3(CO)_8\{InMn(CO)_5\}$	tg	$I4_1/a$	8	1328.3(2) - 3012.3(3)		MnC_5In	OC 184.7(9,20) In[c] 263.5(1)	92.0(5,3.5),171.3(5,2.6) 85.7(3,2.8),179.0(3) -	139
$(n\text{-}Bu_4N)_3[(OC)_3Mn.$ $.(cis\text{-}Nb_2W_4O_{19})]$	trg	R3c	2	1669.6(4)	64.74(2)	MnC_3O_3	OC 184.3(27) O[c] 200.1(12) -	86(1) 98(1,4),173(1)	140

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom.
d The value of C-Mn-Sn angle; C-Mn-P = 94.0(2,5.3)°; Sn-Mn-P = 170.8(1,3.7)°.
e The value of C-Mn-Sn angle; C-Mn-P = 94.0(2,5.7)°; Sn-Mn-P = 170.39(6,3.34)°.
f There are two crystallographically independent molecules.
g The value of Pd-Mn-P angle.
h The Si-Mn-Si = 106.61(6)° and Mn-Mn = 287.1(2)pm.
i The values of C-Mn-Br angles; C-Mn-Se = 90.0(6,3.1) and 175.8(7)°; Se-Mn-Br = 89.3(1,2.5)°; and Br-Mn-Br = 83.4(1)°.
j Mn-Mn = 292.3(2)pm; Ge-Mn-Ge = 107.80(6)°.
k Mn-Mn = 293.4(2)pm; Ge-Mn-Ge = 108.0(1)°.
l Mn-Mn = 305.2(1)pm; Ga-Mn-Ga = 103.14(2,32)°.
m Mn-Mn = 322.7(1)pm; In-Mn-In = 103.64(2,0)°.
n Mn-Mn = 309.1(1)pm; Sn-Mn-Sn = 107.83(2)°.
o Mn-Mn = 308.6(1)pm; SN-Mn-Sn = 108.09(3)°.

There are examples [125-129] containing two manganese and another two central atoms: iron [125], rhodium [126], palladium [127], platinum [117], silicon [128], or selenium [129]. From the bridge viewpoint, the data fall into several groups. For example in the mixed metal, dark blue $[Rh_2(tm4\text{-}br)_4Mn_2(CO)_{10}](PF_6)(Me_2CO)_2$ [126], the dirhodium cation has D_{2d} symmetry capped on each end by a $Mn(CO)_5$ unit with a mean Mn-Rh bond distance of 289.4(5,11) pm, and Mn-Rh-Mn bond angles of 179.3(1)° and 177.0(1)°.

Another molecule [129] consists of two hexacoordinated manganese(I) centres sharing a common edge composed of two bridging bromides plus a bidentate Se-Se bridge. Three fac- carbonyl groups occupy the remaining positions.

There is an example (Table 8) with two different heteroatoms, $[(tpp)SnMn(CO)_4HgMn(CO)_5](CH_2Cl_2)_{0.5}$ [130]. This molecule has an Sn-Mn-Hg-Mn unit, with the Sn-Mn-Hg part bent at a right angle and the Mn-Hg-Mn part almost linear.

The hetero-hexametallic compounds are of five types. In $(\{Mn(CO)_5\}_2In(\mu\text{-}X)_2$ [132], the central cluster consists of a planar In_2X_2 ring with each indium bonded to two manganese atoms, giving a distorted tetrahedral environment around the indium. The manganese has a distorted octahedral environment with the MnC_5In chromophore.

The structure of monoclinic $Mn_2CO_8\{\mu\text{-}Ge(Br)Mn(CO)_5\}_2$ [133] is shown in Figure 11. The central fragment of the molecule consists of a planar Mn_2Ge_2 rhombus with a Mn-Mn distance of 292.3(2) pm across, which is comparable to the value of 293.4(2) pm of the analogous iodo derivative [134]. Both Mn-Mn distances are shorter than those found in $Mn_2CO_8\{\mu\text{-}Sn(X)Mn(CO)_5\}_2$ of 309.1(1)pm(X = Cl) [121] and 308.6(1)pm(X = Br) [137]. This Mn-Mn distance increases with the covalent radius of the bridging hetero-metal atom, 122 pm for Ge and 140 pm for Sn.

In another two isomorphous examples $Mn_2CO_8\{\mu\text{-}Mn(CO)_5\}_2$, where M = Ga or In [135], there is a planar Mn_2M_2 ring in which the Mn-Mn distance increases with the covalent radius of the bridging M atom, from 305.2(1)pm(Ga = 125 pm) to 322.7(1) pm (In = 142 pm).

Orange $H_2Sn_2\{Mn(CO)_5\}_4$ [136] and dark-red $Br_2Sn_2\{Mn(CO)_5\}_4$ [138] have the two connected Sn atoms in tetrahedral environments with two $Mn(CO)_5$ groups and one hydrogen [446] or bromine atom [448]. Each manganese atom is octahedrally surrounded by five carbonyl ligands and a tin atom.

The fifth type is represented by $Fe_2(CO)_8\{InMn(CO)_5\}_2$ [139] which has two types of hetero-metal atom.

Two crystallographically independent molecules, differing by degree of distortion, have been found in $ClSn\{Mn(CO)_5\}_3$ [124]. There are also examples

Table 9 Structural data for manganese compounds with unidintate carbon donor lligands[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore		Mn-L [pm]	L-Mn-L cis- [°] trans- [°]	Ref
$Mn^{II}(CH_2CMe_2Ph)_2(PMe_3)_2$	m	C2/c	4	1888.1(4) 933.0(6) 1635.4(2)	 92.91(2) 	MnC_2P_2	C[b] P	214.9(6,0) 263.3(4,0)	c	141
$Mn^{I}(CO)_5(CH_3)$		Pcmn	4	636.6(2) 1115.1(3) 1195.5(3)		MnC_6				142
$Mn^{I}(CO)_5(CH_3)$						MnC_6	OC H_3C	184.0(4,20) 218.5(11)	94.7(1.0)	143
$Mn^{I}(CO)_5(COCOMe)$	m	2/m	4	632.0(3) 634.0(3) 2997.1(13)	 119.48(3)	MnC_6	OC C	not given not given	92.2-93.5	144
$Mn^{I}(CO)_5(\eta^1-C_2Cl_5)$	m	$P2_1/c$	4	1370.1(2) 875.8(1) 1332.9(1)	 107.78(1) 	MnC_6	OC C	186.3(8,30) 220.4(6)		145
$[cis\text{-}Mn^{I}(CO)_4(COMe)(COPh)].(Me_4N)$	m	$P2_1/c$	4	1034.6(5) 1557.8(7) 1209.4(3)	 100.99(3) 	MnC_6	OC MeOC PhOC	181.9(13,34) 204.5(11) 209.1(11)	92.4(5,4.1) 175.3(3) d_1	146
$Mn^{I}(CO)_4(acp)$	m	C2/c	8	2594.0(7) 599.3(1) 1711.7(4)	 115.63(2) 	MnC_5O	OC (acp)C (acp)O	183.7(3,51) 204.2(2) 205.5(2)	91.9(1,4.7) 169.6(1) d_2	147
$Mn^{I}(CO)_4(acf)$	tr	P1	2	831.0(3) 1057.6(3) 702.6(2)	90.9(3) 105.58(3) 79.26(3)	MnC_5O	OC (acf)C (acf)O	184(4,7) 199(4) 206(4)	not given	148
$Mn^{I}(CO)_4(pfp)$	m	$P2_1/c$	4	954.8(4) 915.4(3) 1820.1(6)	 102.07(2) 	MnC_5N	OC (pfp)C (pfp)N	179.6(10,32) 206.0(8) 207.0(7)	91.7(4,2.5) 172.2(4) e_1	149
$Mn(CO)_4(dmb)$	m	C2/c	8	2736(1) 680.5(4) 1512(1)	 93.30(3) 	MnC_5N	OC (dmb)C (dmb)N	182.6(5,45) 213.9(3) 207.0(7)	91.0(2,3.9) 170.4(2) e_2	150

Table 9, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	Mn-L [pm]		L-Mn-L cis- [°] trans- [°]	Ref
$Mn(CO)_4$(adm)	m	$P2_1/n$	4	1080.3(1) 1381.2(1) 634.7(1)	 93.99(1) 	MnC_5N	OC (adm)C (adm)N	180(-,3) 209.0(9) 198.0(9)	not given	151
$Mn^1(CO)_4$(bhp)	m	C2/c	8	2059.1(3) 2051.7(3) 1246.6(2)	 140.78(2) 	MnC_5N	OC (bhp)C (bhp)N	184.5(7,56) 206.8(5) 212.0(5)	91.88(3,5.3) 167.9(2) e_3	152
$Mn(CO)_4$(top)	m	$P2_1/c$	4	1086.5(3) 1350.8(3) 1657.1(3)	 100.63(2) 	MnC_5P	OC (top)C (top)P	181.9(14,34) 209.7(9) 232.4(3)	92.9(5,5.7) 17.29(5) f_1	153
$Mn(CO)_4$(dpc)	m	C2/c	8	1532.8(29) 1516.6(21) 1585.4(8)	 97.28(10) 	MnC_5P	OC (dpc)C (dpc)P	180.6(8,26) 216.1(9) 229.5(2)	93.1(3,4.4) 166.6(3) f_2	154
$Mn(CO)_4$(dopc)	m	$P2_1/c$	4	814.2(3) 1055.8(3) 2043.1(6)	 100.94(3) 	MnC_5P	OC (dopc)C (dopc)P	183.3(9,35) 211.0(8) 223.7(2)	93.3(4,4.4) 168.5(3) f_3	155
$Mn(CO)_4$(doph)	m	$P2_1/c$	4	1079.9(3) 1202.0(2) 1570.0(8)	 106.36(3) 	MnC_5P	OC (doph)C (doph)P	181.0(14,17) 223.5(11) 228.8(4)	93.2(6,4.6) 165.5(6) f_4	155
$Mn(CO)_4$(topc)	tr	P1	2	825.8(4) 967.3(3) 1352.1(5)	92.32(3) 97.89(4) 107.08(4)	MnC_5P	OC (topc)C (topc)P	182.5(8,32) 218.7(7) 225.2(2)	92.9(4,3.2) 167.7(3) f_5	156
$Mn(CO)_4$(dopo)	m	C2/c	8	2452.9(10) 1393.8(7) 1246.4(7)	 116.58(5) 	MnC_5P	OC (dopo)C (dopo)P	182.3(10,39) 220.0(8) 227.9(3)	not given 176.8(4) f_6	157
$Mn(CO)_4$(popc)	m	$P2_1/c$	4	913(2) 1371(2) 1646.4(3)	 115.39(2) 	MnC_5P	OC (popc)C (popc)P	not given 221.0(3) 227.1(1)	not given 164.9(2) f_7	158

Table 9, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	Mn-L [pm]		L-Mn-L cis- [°] trans- [°]	Ref
$Mn(CO)_4(dph)$	tr	P1	2	912.4(2) 971.8(2) 1313.0(2)	75.07(3) 108.80(3) 111.79(3)	MnC_5P	OC (dph)C (dph)P	181.7(7,24) 220.2(5) 232.8(2)	92.2(3,5.2) 165.7(3) f_8	159
$Mn^I(CO)_4(CH_2COCH_3)(PPh_3)$	m	$P2_1/c$	4	671.9(1) 1408.3(4) 1477.8(4)	 100.63(2) 	MnC_5P	OC C P	182.2(6,45) 221.0(5) 234.3(1)	93.1(3,5.8) 165.0(3) f_9	160
$Mn^I(CO)_4(CH_3)(PPh_3)$[g]	or	$P2_12_12_1$	8	1116(2) 3421(1) 1109(2)	 	MnC_5P MnC_5P	OC H_3C P OC H_2C P	179(8,40) 230(6) 231.1(18) 174(8,15) 195(6) 231.5(18)	93(4,7),169(4) f_{10} 94(3,8),162(3) f_{11}	161
$Mn(CO)_4(dpch)$	or	$P2_12_12_1$	4	1476.6(8) 1529.2(3) 857.0(2)	 	MnC_5P	OC (dpch)C (dpch)P	182.3(9,25) 222.2(10) 230.3(2)	93.7(4,6.2) 164.8(4) f_{12}	162
$Mn(CO)_4(mdpc)$	m	$P2_1/c$	4	845.2(2) 1475/8(6) 1598.6(6)	 103.78(2) 	MnC_5P	OC (mdpc)C (mdpc)P	180.6(10,16) 223.7(9) 228.0(2)	93.1(4,3.7) 169.7(4) f_{13}	162
$Mn(CO)_4(C_2PPh_3)(Br)$	m	$P2_1/c$	4	956.4(3) 1201.9(3) 2123.7(8)	 107.02(2) 	MnC_5Br	OC C Br	182-187 199 not given	not given	163
$Mn(CO)_4(dac)$	m	C2/c	8	1545.7(6) 1541.9(1) 1593.4(3)	 96.49(3) 	MnC_5As	OC (dac)C (dac)AS	182.0(7,18) 217.3(8) 237.8(1)	93.0(3,4.8) 167.8(3) h	164
$Mn(CO)_4(mtpc)$	m	C2/c	8	2434.9(6) 1438.2(4) 1032.1(9)	 108.99(4) 	MnC_5S	OC (mtpc)C (mtpc)S	183.3(12,25) 204.9(8) 240.6(4)	91.8(5,2.3) 173.0(4) i	165
$Mn^{IV}(CH_3)_4(dmpe)$	m	$P2_1/c$	4	1398.6(2) 1311.2(2) 867.7(1)	 96.44(2) 	MnC_4P_2	H_3C P	209.9(11,39) 244.9(4,2)	93.6(5) j	166

Table 9, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	Mn-L [pm]	L-Mn-L cis- [°] trans- [°]	Ref
$Mn(CO)_3(obdp)$	tr	$P\bar{1}$	2	930 1169 1065	81.91 96.64 83.72	MnC_4OP	OC 178(1,1) (obdp)O 207.0(6) (obdp)P 229.9(2)	not given	167
$Mn(CO)_3(obdp)$	or	Pbca	8	1595 1718 1628		MnC_4OP	OC 179.1(10,28) (obdp)O 206.7(7) (obdp)P 229.5(3)	not given	167
$Mn(CH_3)_2(dmpe)_2$	m	$P2_1/n$	2	957.6(2) 1264.2(3) 895.3(2)	 90.13(2)	MnP_4C_2	H_3C 220(2) P 224.6(5,5)		167a
Mn(CO)(acdpe)(dpe)	tr	$P\bar{1}$	2	1060(1) 1337(1) 1962(1)	99.1(1) 98.1(1) 112.3(1)	MnP_4C_2	OC 173 C 205 P 228	82(-,1)	168
$Mn(CO)_3\{OC(H)HCNP\}.$ $.\{P(OPh)_3\}$	or	Pbca	8	1806.3(7) 1844.6(8) 2500.3(7)					169
$Mn(CO)_3(PPh_3)(msp)$	tr	$P\bar{1}$	2	1102.2(7) 1348.5(9) 912.3(6)	94.52(1) 109.90(1) 98.14(1)	MnC_4PS	OC 179.4(6,14) (msp)C 206.4(5) (msp)S 231.0(4) Ph_3P 238.2(4)	89.2(2,2.6) k	170
$\{Mn(CO)_2(dpe)\{(NC)_2C=CP(O)\}.$ $.(OCHMe_2)_2\}$	m	$P2_1/n$	4	1741.9(4) 1256.0(3) 1816.4(9)	 109.10(4)	MnC_3P_2O	OC not given C 195.7 O 215.7 (dpe)P 232.0(-,15)	1	171

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c C-Mn-N = 137.9(1)°; C-Mn-P = 95.3(2) and 112.9(2)°; P-Mn-P = 96.2(2)°.
d_1 OC-Mn-COMe = 88.4(5,3.5) and 173.2(5)°; OC-Mn-COPh = 90.2(5,5.3) and 170.1(5)°; MeOC-Mn-COPh = 81.2(4)°.
d_2 OC-Mn-C(acp) = 89.3(1,7.5) and 169.1(1)°; OC-Mn-O(acp) = 91.2(1,2.2) and 175.5(1)°; (acp)C-Mn-O(acp) = 79.4(1)°.
e_1 OC-Mn-C(pfp) = 88.5(4,4.7) and 175.0(4)°; OC-Mn-N(pfp) = 91.9(4,3.7) and 172.6(4)°; (pfp)C-Mn-N(pfp) = 79.4(3)°.
e_2 OC-Mn-C(dmb) = 88.4(2,4.2) and 174.2(2)°; OC-Mn-N(dmb) = 93.0(2,20) and 172.7(2)°;(dmb) C-Mn-N(dmb) = 80.2(2)°.

Footnotes for Table 9 (continued)

e_3 OC-Mn-C(bhp) = 86.1(2,4.1) and 177.6(3)°; OC-Mn-N(bhp) = 93.7(2,8.7) and 169.5(2)°; (bhp) C-Mn-N(bhp) = 79.3(2)°.
f_1 OC-Mn-C(top) = 88.6(5,4.1) and 168.7(5)°; OC-Mn-P(top) = 93.3(3,7.9) and 159.9(5)°; (top)C-Mn-P(top) = 67.5(3)°.
f_2 OC-Mn-C(dpc) = 86.8(4,3.4) and 174.6(3)°; OC-Mn-P(dpc) = 91.3(2,1.8) and 171.4(3)°; (dpc)C-Mn-P(dpc) = 81.7(3)°.
f_3 OC-Mn-C(dope) = 88.8(4,8.5) and 164.8(4)°; OC-Mn-P(dope) = 92.7(3,6.2) and 163.4(3)°; (dope)C-Mn-P(dope) = 66.1(3)°.
f_4 OC-Mn-C(doph) = 82.7(5,2.0) and 173.5(5)°; OC-Mn-P(doph) = 89.9(4,1.6) and 178.1(5)°; (doph)C-Mn-P(doph) = 95.9(3)°.
f_5 OC-Mn-C(topc) = 83.8(3,7) and 173.9(3)°; OC-Mn-P(topc) = 90.1(3,2.9) and 176.3(3)°; (topc)C-Mn-P(topc) = 93.1(2)°.
f_6 OC-Mn-C(dopo) = 87.0(4)°; OC-Mn-P(dopo) 92.6(3,3.9) and 168.6(3)°; (dopo)C-Mn-P(dopo) = 81.9(2)°.
f_7 (pope)C-Mn-P(popc) = 92.1(1)°.
f_8 OC-Mn-C(dph) = 85.9(3,5.4) and 174.6(3)°; OC-Mn-P(dph) = 91.5(3,3.9) and 176.8(2) (dph)C-Mn-P(dph) = 86.9(2)°.
f_9 OC-Mn-C = 85.7(2,5.8) and 178.5(2)°; OC-Mn-P = 89.0(2,9) and 177.1(2) C-Mn-P = 90.9(1)°.
f_{10} OC-Mn-CH_3 = 82(3,5) and 172(2)°; OC-Mn-P = 92(3,4) and 169(2)°; H_3C-Mn-P = 93(2)°.
f_{11} OC-Mn-CH_3 = 82(3,5) and 173(3)°; OC-Mn-P = 89(2,3) and 178(2)°; H_3C-Mn-P = 98(2)°.
f_{12} OC-Mn-C(dpch) = 83.4(4,1.6) and 175.7(4)°; OC-Mn-P(dpch) = 89.9(3,2.7) and 175.6(3)°; (dpch)C-Mn-P(dpch) = 90.8(2)°.
f_{13} OC-Mn-C (mdpc) = 86.0(4,2.1) and 177.2(3)°; OC-Mn-P(mdpc) = 90.8(3,4.2) and 170.3(3)°; (mdpc) C-Mn-P(mdpc) = 82.2(2)°.
g These are crystallographically independent molecules.
h OC-Mn-C(dac) = 86.4(3,4.9) and 174.4(3)°; OC-Mn-As = 90.9(2,2.2)°; C-Mn-As = 81.3(2)°.
i OC-Mn-C(mtpc) = 89.4(4,5.4) and 175.1(4)°; OC-Mn-S(mtpc) = 88.5(4,2.0) and 177.2(4)°; (mtpc)C-Mn-S(mtpe) = 90.5(4)°.
j P-Mn-P = 80.2(2)°; P-Mn-C = 89.6(4,3.7)°.
k OC-Mn-C(msp) = 87.3(2,3.9) and 172.9(2)°; OC-Mn-P = 95.2(2,2.2) and 172.6(2)°; OC-Mn-S = 94.2(2,7) and 174.1(2)°; (msp)C-Mn-P = 89.2(2)°; (msp)C-Mn-S = 82.9(2)°; P-Mn-S = 86.2(1)°.
l At 253K.

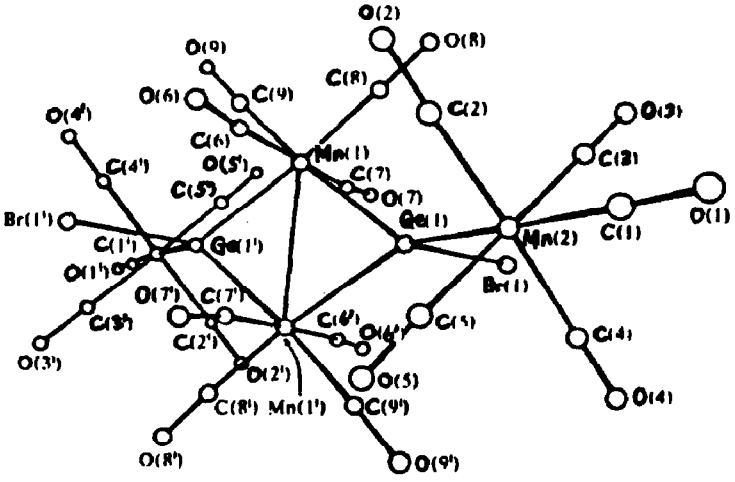

Figure 11. Structure of $Mn_2(CO)_8\{\mu\text{-}Ge(Br)Mn(CO)_5\}_2$
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with non-equivalent chromophores: MnC_5S and MnC_3S_2Fe [125]; MnC_5Pd and MnC_4PPd_2 [127]; MnC_5M and MnC_4M_2 [121,133-135,137]

The mean Mn-CO bond distance increases from 181.2 pm in the hetero-tetrametallic compounds to 183.9 pm in the hetero-hexametallic compounds. The former is comparable to that found for the hetero-trimetallics (181.6 pm, Table 7), and the latter with the value for the hetero-bimetallics (183.6 pm, Table 6).

3. MANGANESE ORGANOMETALLIC COMPOUNDS

(A) Mononuclear Compounds

1. Manganese compounds with unidentate carbon ligands

Crystallographic and structural data for these derivatives are given in Table 9, and are listed and referenced in order of increasing coordination number and increasing atomic number of the principal coordinated atom.

Colourless high-spin $Mn^{II}(CH_2CMe_2Ph)_2(PMe_3)_2$ [141] is the only example in which the manganese(II) atom has a distorted tetrahedral geometry with C-Mn-C and P-Mn-P angles of 137.9(1)° and 96.2(1)°, respectively, which reflect the relative sizes of the two kinds of ligand. In all other examples the manganese atoms are in octahedral environments. The crystal structure of yellow cis-

$[Mn(CO)_4(COMe)(COPh)](Me_4N)$ [146] is shown in Figure 12 as an example. The manganate anion has acetyl (Mn-C = 204.5(11)pm) ligands in cis positions and the remaining four sites are occupied by carbonyl ligands (Mn-C = 181.9(13,34)pm). The Mn-C(COMe) distance is somewhat shorter than Mn-C(COPh), reflecting the steric hindrance.

There is no example in Table 9 with six equivalent ligands. Only two examples have a non-carbon bonded tridentate ligand, bidentate ligands being more common. Distortion isomerism is observed for $Mn(CO)_3$ (obdp) [167] which exhibits two isomers, triclinic and orthorhomic with differences in degree of distortion. The two crystallographically independent molecules found in $Mn(CO)_4$-$(CH_3)(PPh_3)$ [161] are another example of distortion isomerism.

2. Compounds with bi-,tri- or tetradentate carbon ligands

Crystallographic and structural data for these compounds are found in Table 10, in which coordination numbers of four, six, seven and eight are observed. There is only one example, $[Mn(tpbp)_2](thf)_2$ [172], of a high spin manganese(II) atom with a distorted tetrahedral environment.

There are two examples, $[Mn(CO)_4(Ph\text{-}CHOCOCO)](ppn)$ [173] and $Mn[\sigma$-$(CH_2)_2C_6H_4](dmpe)_2$ [141], with manganese coordination number six. In the latter, the low spin manganese(11) atom is in a slightly distorted octahedral environment due mainly to the bite restrictions of the three chelating ligands, with P-Mn-P

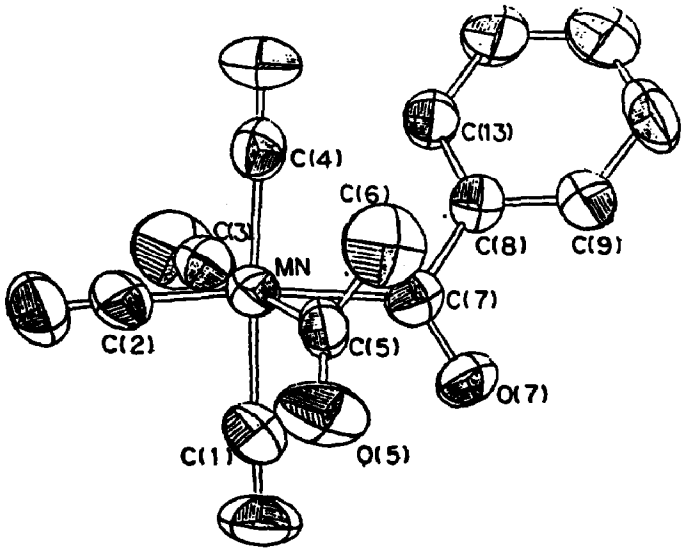

Figure 12. Structure of the cis-$[Mn(CO)_4(COMe)(COPh)]^-$ Ion
Reproduced with permission from J. Amer. Chem. Soc. [146]

Table 10 Crystallographic and structural data for manganese organometallic compounds with a multidentate ligands[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore		Mn-L [pm]	L-Mn-L L-Mn-L' [°]	Ref
$[Mn^{II}(tpbp)_2](thf)_2$	m	C2/c	4	2848.5(5) 1298.0(2) 1968.9(2)	 110.51(1) 	MnC_4	C[b] C	224.9(17,14) 279.8(20,0)	84.0(7)	172
$[Mn(CO)_4(Ph\text{-}CHOCOCO)]^-$[c] .(ppn)	tr	P$\bar{1}$	2	1001.6(4) 1577.2(5) 1569.8(4)	86.55(3) 89.09(3) 118.62(3)	MnC_6	OC C	182.2(8,6) 202.3(7,11)	93.47(33,2.13),170.85(34) 88.29(31,3.61),172.91(32,33)	173
$Mn^{II}\{o\text{-}(CH_2)_2C_6H_4\}(dmpe)_2$	m	$P2_1/c$	4	915.3(8) 1600.1(2) 1728.2(4)	 103.66(3) 	MnP_4C_2	C P	210.7(6,3) 226.4(3,34)	84.7(2) d	141
[cis-$Mn(CO)_4(\eta^3\text{-dik})$](ppn)	m	$P2_1/c$	4	1457.3(4) 1747.2(4) 2017.5(5)	 123.03(2) 	MnC_7	OC C	180(2,5) 225(2,13)	90.7(7,7.5),168.3(6) 97.1(7,15.1),150.4(8)	174
$Mn(CO)_3(C_{15}H_{22}O_6P)$	m	$P2_1/m$	2	842.6(2) 1622.1(4) 864.8(2)	 116.62(2) 	MnC_7	OC C C	179.0(10,21) 205.0(7)(2x) 215.8(8)(2x)	91.0(4,1.3) e_1	175 176
$Mn(CO)_3(C_{14}H_{21}O_6PS)$	tr	P$\bar{1}$	2	902.3(2) 1692.1(3) 867.0(2)	102.01(2) 94.87(2) 90.68(2)	MnC_7	OC C C	180.7(3,9) 207.7(2,5) 214.1(3,10)	91.4(1,5.2) e_2	175 177
$Mn(CO)_3(\eta_3\text{-}C_3H_5)CNMe)$[f]	m	Pa	4	709.2(3) 2432(19) 594.8(2)	 107.55(20) 	MnC_7	OC $(n_3)C$ NC	179.7(9,113) 217.3(1,58) 194.2(7)		178
						MnC_37	OC $(n_3)C$ NC	177.8(10.56) 219.0(1,78) 191.3(7)		
$Mn(CO)_3\{\eta^4\text{-}(C_4F_6)_2SC_6F_5\}$	tr	P$\bar{1}$	2	788.9(6) 1173.7(8) 1219.5(9)	91.45(10) 69.71(10) 81.55(9)		OC C	not given not given		179

Table 10, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	L-Mn-L L-Mn-L' [°]	Ref
$Mn(CO)_3\{\eta^4\text{-}C_4F_6)_2SC_6F_5\}$	tr	$\bar{P}1$	2	788.9(6) 1173.7(8) 1219.5(9)	91.45(10) 69.71(10) 81.55(9)	MnC_7	OC not given C not given		179
$Mn(CO)_2(\eta^4\text{-}C_4Ph_4)(NO)$	m	$P2_1/c$	4	892.1(2) 1877.5(8) 1405.6(5)	 92.27(3)	MnC_6N	OC 184(1) ON g (η_4)C 211(1,3)	g	180
$Mn(CO)_3(\eta^4\text{-}C_4H_3S.CN)$	m	$P2_1/C$	4	1200.8(2) 669.35(8) 1217.2(2)	 95.63(2)	MnC_6S	OC 179.7(6,6) C 211.9(6,76) S 234.6(2)	93.6(2,6.1) h	181
$Mn^1(CO)_2(\eta^2\text{-}C_3H_5)\{P(OMe)_3\}_2$	m	$P2_1/a$	4	1861.8(11) 921.8(7) 1060.7(11)	 102.1(1)	MnC_5P_2	OC 179(2,4) (η^3)C 218.9(15,75) P 219.7(5,22)	97.7(7) i	182
$Mn(CO)_3$(mopp)	tr	$\bar{P}1$	2	930.3(5) 1168.9(6) 1065.4(6)	81.90(2) 96.64(2) 83.71(2)	MnC_5OP	OC 179.0(4,10) C 221.8(3,2) O 205.8(2) P 230.0(1)	91.78(18,6.51) j	183
$Mn(\eta^3\text{-}C_5H_8)dmpe)_2$	m	$P2_1/n$	4	1060.6(4) 2331(1) 901.9(2)	 94.74(2)	MnC_3P_4	C 220(2,10) P 223.3(10,27)	37.5(6,1.5),68.1(7) k	184
$Mn(CO)_3\{\eta^5\text{-}C_6H_6(CH_3)\}$	m	$P2_1/c$	4	654.6(4) 981.8(3) 1725.0(5)	 112.00(3)	MnC_7H	OC 179.8(3,23) C 215.4(3,147) H 186(2)	92.9(1,7.9) l	185
$Mn(CO)_3(\eta^5\text{-min})$	m	C2/c	8	2546 1162 825	 109.8	MnC_7N	OC 172(-,6) C 216(-,6) N 216	92(-,2) m	186

Table 10, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromo-phore	M-L [pm]	L-Mn-L L-Mn-L' [°]	Ref
$Mn(CO)_3(\eta^5\text{-mpc})$	m	$P2_1/n$	4	2099.5(5) 1086.9(3) 678.4(2)	 90.17(3) 	MnC_7P	OC 178.9(9,12) C 215.9(8,17) P 237.9(2)	92.3(4,1.6) n	187
$Mn(CO)_3\{\eta^5\text{-}C_4As(Ph)_4\}$	m	$P2_1/c$	4	883 1112 2672	 98.09 	MnC_7As	OC not given C 219.3(5) As 249.2(2)		188

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c At 113(5)K.
d P-Mn-P = 83.3(1,1)° and C-Mn-P = 88.6(2,5.4)°.
e_1 OC-Mn-C = 98.2(3)(2x); 104.7(4)(2x) and 161.5(3)°(2x); and C-Mn-C = 69.7(2)°.
e_2 OC-Mn-C = 94.8(1,1); 101.5(1,1.5) and 164.4(1,9)°; and C-Mn-C = 80.1(1)°.
f There are two crystallographically independent molecules.
g Cannot distinguish between Mn-CO and Mn-NO bond distances of 172(1) and 178(1)pm; OC-Mn-X (X = CO or NO) = 99.7(5,9)°; and X-Mn-X = 99.4(5)°.
h The OC-Mn-C = 91.6 - 163.5(2)°; OC-Mn-S = 101.2(2,3.1) and 160.6(2)°; C-Mn-C = 37.2(3,1.4) and 65.5(2)°; and C-Mn-S = 46.4(2) and 70.1(2,1)°.
i OC-Mn-C = 97.6(6,1.5) and 164.3(7,1.9)°; OC-Mn-P = 86.9(6,3)°; C-Mn-C = 67.0(6)°; C-Mn-P = 93.1(5,12.0)°; and P-Mn-P = 172.8(2)°.
j OC-Mn-C = 98.93(16), 130.30(15,2.25) and 164.94(15)°; OC-Mn-O = 100.51(14,17) and 159.66(13)°; OC-Mn-P = 89.09(12,1.03) and 176.25(14)°; C-Mn-O = 36.01(11) and 66.03(10)°; C-Mn-P = 91.80(9,8.34)°; O-Mn-P = 83.25(7)°; and C-Mn-C = 38.28(12)°.
k C-Mn-P = 95.2(6,7.6) and 162.5(5,6.4); and P-Mn-P = 89.1(3,10.2) and 169.3(3)°.
l OC-Mn-C = 90.9(1) - 166.6(1)°; OC-Mn-H = 88,.8(7,1.1) and 175.2(6)°; C-Mn-C = 38.9(1,6) and 70.4(1,2.0)°. and C-Mn-H = 27.4(7) - 91.9(7)°.
m OC-Mn-C = 90 - 160°; and OC-Mn-N = 97,107 and 158°.
n C-Mn-C = 38.2(3,3)°; and C-Mn-P = 45.5(2,9)°.

angles of 83.2(1)° and 83.3(1)° and a C-Mn-C angle of 84.7(2)°. The mean Mn-C bond distance of 210.7(6,3) pm is about 15.7 pm shorter than the mean Mn-P distance (226.4(3,34)pm), reflecting the van der Waals radii of carbon (170 pm) and phosphorus (185 pm).

In another ten examples [174-184) manganese is bonded to seven donor atoms. There are various stereochemical arrangements: four unidentate and one carbon bonded tridentate ligand [174,178,182]; three unidentate ligands and one tetradentate carbon bonded ligand [175-177,179,180]; three unidentate ligands and one tetradentate (3C+S) [181]; three unidentate ligands and one tetradentate (2C+O+P) [183]; two bidentate ligands and one tridentate carbon bonded ligand [184]. The molecular structure of orange $Mn(CO)_2\eta^4\text{-}C_4Ph_4(NO)$ [180] is shown in Figure 13 as an example.

The tetraphenylcyclobutadiene ligand is η^4 coordinated to the Mn atom at an average Mn-C distance of 211(1,3) pm. The Mn-C(2), (CO) bond distance is 184(1) pm and another two of the X-O(X = C or N) ligands are disordered (Mn-X = 172(1) and 178(1) pm). The disorder problem has been addressed in the original literature [180] and need not be elaborated upon here. Two crystallographically independent molecules have been found in $Mn(CO)_3(\eta^3\text{-}C_3H_5)(CNMe)$ [178], as examples of distortion isomerism.

Comparing two types of seven coordination (a) four unidentate + one tridentate C-ligand systems with (b) three tridentate + one tetradentate, the

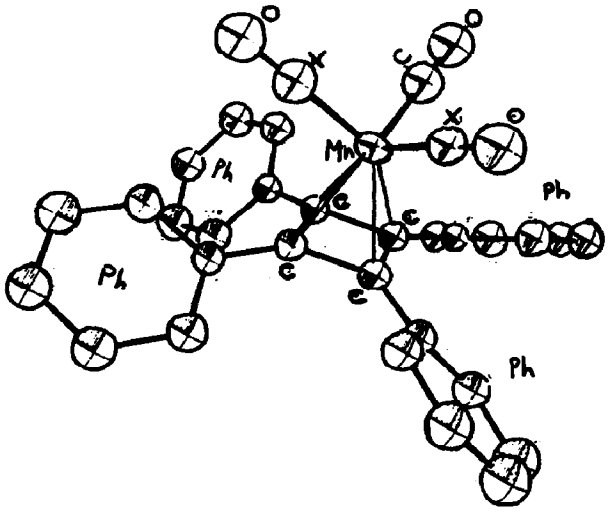

Figure 13. Structure of $Mn(CO)_2(\eta^4\text{-}C_4Ph_4)(NO)$
Reproduced with permission from Organometallics [180]

Table 11 Crystallographic and structural for manganese compounds with penta- or hexadentate carbon ligand[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$Mn^{I}(CO)_3(\eta^5\text{-cp})$	m	$P2_1/a$	4	1207.7(3) 705.7(2) 1091.3(2)	 117.68(2) 	MnC_6	OC[b] 178.0(2,8) (cp)C 212.4(2,7)	92.02(9,50) c	189
$Mn(CO)_3(\eta^5\text{-cpac})$	m	$P2_1/c$	4	1319 1239 626	 95 	MnC_6	OC 180(5,3) (cp)C 214(5)	91.94(2.0,3.21)	190 191
$Mn(CO)_3(\eta^5\text{-cp-bz})$	m	$P2_1/c$	4	1247 642 1649	 96.7 	MnC_6			191
$Mn(CO)_3(\eta^5\text{-cp-mc})$						MnC_6	OC 174.6 (cp)C 212	not given	192
$Mn(CO)_3(\eta^5\text{-cp-ae})$	m	$P2_1$	2	812.0(1) 944.25(8) 857.6(1)	 93.70(1) 	MnC_6	OC 177(1,2) (cp)C 214(1,1)	91.1(6,9)	193
$Mn(CO)_3(\eta^5\text{-cp-df})$	or	$P2_12_12_1$	4	746.1(1) 765.2(1) 2469.6(4)	 	MnC_6	OC 180.2(3,5) (cp)C 214.6(3,25)	91.9(1,6)	
$Mn(CO)_3(\eta^5\text{-dop})$	m	$P2_1/c$	4	1324.9(5) 717.8(4) 1566.2(6)	 96.66(3) 	MnC_6	OC 181(1,6) C 219(1,11)	93.1(6,6.3) d	
$Mn(CO)_3(\eta^5\text{-cp-tm})$	m	$P2_1/n$	4	799.6(3) 250.0(1) 1048.6(4)	 96.18(2) 	MnC_6	OC 176.7(13,10) C 215.8(10,66)	90.6(6,3) 38.7(3,5)	196
$Mn(CO)_3(\eta^5\text{-}C_9H_8Br)$	m	$P2_1/c$	4	1295.3(9) 762.7(5) 1309.8(9)	 110.53(5) 	MnC_6	OC 179.3(10,23) C 216.2(9,60)	92.1(5,1.2)	197
$Mn(CO)_2(\eta^5\text{-cp})(CNBu)$	or	$Pna2_1$	4	1912.3(9) 602.0(3) 1094.2(5)	 	MnC_6	OC 187(4,5) (cp)C 214(3,60 C 185(2)	91(1) 92(2,2)	198

Table 11, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$Mn(CO)_2(\eta^5\text{-cp})(CMe_2)$[f]	or	$Cmc2_1$	8	985.8(1) 1212.1(1) 1653.7(1)		MnC_6	OC 179.2(4,0) (cp)C 218.2(8,9) C 187.2(10)	88.5(2) 90.5(3)	199
						MnC_6	OC 179.3(5,0) (cp)C 219.3(8,4) C 186.4(10)	89.0(2) 90.7(3)	
$[Mn(CO)_2(\eta^5\text{-cp})(COPh)]$. .$(NMe_4)$[f]	or	Ib2a	16	5826.6(7) 1137.2(3) 1068.3(2)		MnC_6	OC 178(3,1) (cp)C 215(4,3) C 195(2)	90.7(1.2) 87.6(1.4,1.2)	200
						MnC_6	OC 179(3,2) (cp)C 219(4,3) C 197(2)	88.8(1.2) 88.1(1.2,3.9)	
$Mn(CO)_2(\eta^5\text{-cp})\{C(OEt)$. .Ph$\}$	m	$P2_1/c$	4	756.0(3) 722.8(4) 2652(1)	94.11(4)	MnC_6	OC 180.0(15,5) (cp)C 216.9(14,19) C 186.5(14)	91.1(7)	
$Mn(CO)_2(\eta^5\text{-cp})\{C(F)Ph\}$	m	$P2_1/c$	4	1304.5(6) 753.1(2) 1236.0(5)	92.87(3)	MnC_6	OC 179.0(6,6) (cp)C 214.8(7,12) C 183.0(5)	90.8(3) 91.9(3,1.9)	202
$Mn(CO)_2(\eta^5\text{-cp})(CPh_2)$	m	$P2_1/c$	4	1288.2(2) 738.0(2) 1724.3(2)	106.95(1)	MnC_6	OC 178.8(2,5) (cp)C 217.2(2,19) C 188.5(2)	90.80(9) 92.45(9,1.60) g	203
$Mn(CO)_2(\eta^5\text{-cp})(C{=}CMe_2)$	or	Pnma	4	742.3(5) 1171.2(9) 1236(1)		MnC_6	OC 174(1,0) (cp)C 213(2,2) C 179(2)	87.7(7) 91.5(8)	204
$Mn(CO)_2(\eta^5\text{-cp})(CCPMe_2$. .Ph)	m	$P2_1/a$	4	1061.1(2) 1860.3(3) 819.3(2)	102.55(2)	MnC_6	OC 174.3(7,1) (cp)C not given C 189.5(5)	not given	205
$Mn(CO)_2(\eta^5\text{-cp})(C{=}CHPh)$	or	Pccn	8	1049.2(2) 3303.8(6) 747.5(2)		MnC_6	OC 174(3,7) (cp)C 216(2,0) C 168(2)	89(1) 92(1)	206

Table 11, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ¥[°]	Chromophore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$[Mn(CO)_2(\eta^5\text{-cp}).(CCHCPh_2)](BF_4)$ [h]	m	$P2_1/c$	4	1017.9(3) 1528.6(4) 1296.1(4)	 103.57(3) 	MnC_8	OC 174.1(5,76) (cp)C 213.9(6,24) C 183.8(6)	93.1(2) 94.5(3,6)	207
$[Mn(CO)_2(\eta^5\text{-cp})\{C(PPh_3).CCPh_2\}]CH_2Cl_2$	tr	$P\bar{1}$	2	1026.6(2) 1060.3(2) 1632.0(4)	79.22(2) 84.30(2) 74.70(2)	MnC_8	OC 176.5(2,2) (cp)C 215.3(2,13) C 206.5	90.4(1) 96.2(1,4.4)	208
$Mn(CO)_2(\eta^5\text{-cp})\{C(Ph).COPh\}$	m	$P2_1/n$	4	711(2) 1087(2) 2194(2)	 93.5(2) 	MnC_6	OC not given (cp)C not given C 188(2)		209
$Mn(CO)_2(\eta^5\text{-cp}).\{C(CO_2Me)CHPPh_3\}$ [h]	m	$P2_1/a$	4	1474(1) 1091(1) 1557(1)	 100.57(5) 	MnC_8	OC 176.5(4,5) (cp)C 215.8(3,6) C 198.5(3)	95.7(1) 88.6(2,3.1)	210
$Mn(CO)_2(\eta^5\text{-cp}).(CCHC_6H_4CBrCH_2)$	or	$P2_12_12_1$	4	692.5(1) 855.9(1) 2658.9(2)	 	MnC_8	OC 176(2,1) (cp)C 214(3,4) C 180(3)	91(1) 90(1,0)	211
$Mn(CO)_2(\eta^5\text{-cp})(dbc)$	m	$P2_1/n$	4	1045.6(4) 789.9(2) 2153.6(4)	 101.56(3) 	MnC_8	OC 178.4(6,6) (cp)C not given C 185.3(5)	88.9(3) 93.9(3,6)	212
$Mn'(CO)_2(\eta^5\text{-cp})(dca)$	m	$P2_1/c$	4	1178(2) 999.4(1) 1806(4)	 110(1) 	MnC_8	OC 176.7(7,4) (cp)C 212(1,1) C 180.6(6)	87.9(3) 90.9(3,3)	213
$Mn(CO)_2(\eta^5\text{-cp})(acn)$	m	$P2_1/a$	4	925.7(4) 1252.8(5) 1215.6(4)	 91.44(3) 	MnC_7N	OC 177.0(4,2) (cp)C 215.0(5,39) (acn)N 206.3(3)	90.1(2) 95.7(1,1.8)	214
$Mn(CO)_2(\eta^5\text{-cp})(dam)$	m	$P2_1/n$	4	1019.85(44) 1405.50(74 1105.30(52)	 116.22(3) 	MnC_7N	OC 179.7(7,12) (cp)C 213.9(7,14) (dam)N 179.6(5)	90.3(3) 94.8(3,1.4)	215

Table 11, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromo-phore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$[Mn(CO)_2(\eta^5\text{-cp}^*).(o\text{-}N_2C_6H_4CF_3)](BF_4)$	or	Fdd2	16	1286.6(3) 5660.5(11) 996.4(2)		MnC_7N	OC 182.9(13,14) (cp*)C 213.8(11,34) N 169.3(7)	89.1(6) 98.8(5,5)	216
$Mn^1(CO)_2(\eta^5\text{-cp})(PPh_3)$	tr	P$\bar{1}$	2	941(2) 1060(2) 1136(2)	103.47(16) 79.47(16) 101.72(16)	MnC_7P	OC 175.3(11,13) (cp)C 214.5(12,22) P 223.6(3)	92.42(41) 91.59(30,1.07)	217
$Mn^1(CO)_2(\eta^5\text{-cp}^*)(PPh_3)$	or	Pbca	8	775.5(3) 1697.5(7) 3309.1(11)		MnC_7P	OC 177(1,1) (cp*)C 214.7(9,15) P 223.2(2)	91.5(4) 92.7(3,1.4)	218
$Mn^1(CO)_2(\eta^5\text{-cp})(pvp)$	tr	P$\bar{1}$	2	1272(1) 989(1) 1112(1)	94.10(8) 116.90(8) 70.28(8)	MnC_7P	OC 176(2,1) (cp)C 210-215 P 220.1(4)	not given	219
$[Mn^1(CO)(\eta^5\text{-cp}).\{CS_2C_2\{P(OMe)_3\}]$	m	$P2_1/c$	4	785.2(2) 2296.2(5) 1200.2(3)	108.42(2)	MnC_7P	OC 175.4(3) (cp)C 215.5(3,21) C 187.6(2) P 217.4(0)	i	220
$Mn(CO)_2(\eta^5\text{-cp})(SO_2)$	m	$P2_1/c$	4	1098(2) 1063(2) 743(2)	100.75(8)	MnC_7S	OC 174.9(15,39) (cp)C 209.1(17,25) S 203.7(5)	90.55(62) 92.91(50,1.95)	221
$Mn(CO)_2(\eta^5\text{-cp}).(SC_{11}H_{18})$	m	$P2_1/n$	4	822.9(2) 1045.1(2) 2084.1(3)	93.64(1)	MnC_7S	OC 177.7(3) (cp)C 214.3(4) S 221.8(1)	89.1(1) 94.1(1,5)	222
$Mn(CO)(\eta^5\text{-cp}^*)(NO).(PPh_3)$	or	Pbca	8	1796.9(53) 2663.1(78) 927.7(35)		MnC_6NP	OC 177.1(7) (cp)C 212.6(6,67) (cp)C 269.3(6) ON 167.4(5) Ph_3P 228.5(2)	j	223

Table 11, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$Mn(CO)(\eta^5\text{-cp}^*)(NO)I$	m	$P2_1/a$	4	1281.1(9) 807.8(8) 1243.5(18)	 126.90(3) 	MnC_5NI	OC 180.3(6) (CP)C 215.9(6,30) ON 164.7(6) I 264.5(2)	k	224
$Mn(tmeda)(\eta^5\text{-cp})(\eta^1\text{-cp})$	m	$P2_1/n$	4	1237.4(3) 969.4(1) 1342.3(1)	 101.24 	MnC_5N_2	(η^1)C 232.0(5) (η^5)C 250.7(7,64) N 234.6(5,8)	l	225
$Mn(CO)_3(\eta^5\text{-}C_8H_7)$	or	Pnma	4	1319.9(10) 881.0(7) 752.8(6)	 	MnC_8	OC 179.1(9,11) (η^5)C 217.7(8,42)	92.0(4,2.6)	226
$[Mn^1)(CO)_3(\eta^5\text{-exo-}$ $\text{-}PPh_3C_7H_8)](BF_4)$	m	$P2_1/c$		959(3) 1458.0(4) 1957.4(6)	 107.23(8) 	MnC_8	OC 180.0(6,4) C 216.0(7,45)	92.5(2,5.9)	227
$Mn(CO)_2(\eta^5\text{-cp}).$ $(\eta^2\text{-}C_{17}H_{14}O$	m	$P2_1/n$	4	998.9(3) 1302.3(4) 1466.6(4)	 91.33(4) 	MnC_9	OC 179.5(9,15) (cp)C not given (η^2)C 194.0(7) (η^2)C 221.2(6)	not given	212
$Mn(CO)_2(\eta^5\text{-cp}).^m$ $.(\eta^2\text{-}C_7H_8)$	or	Pnma	4	1198.6(5) 1117.1(5) 883.7(5)	 	MnC_9	OC 177.3(2,0) (cp)C 213.1(3,10) (η^2)C 215.4(2,0)	91.4(5) m	228
$Mn(CO)_2(\eta^5\text{-cp})(\eta^2\text{-dep})^f$	tr	P1	4	1057.8(2) 1112.0(2) 1806.9(4)	72.42(1) 84.46(1) 88.02(1)	MnC_9 MnC_9	OC 175.9(7,14) (cp)C 215.8(6,9) (η^2)C 211.9(9,22) OC 178.1(7,3) (cp)C 215.5(5,14) (η^2)C 212.3(8,22)	n_1 n_2	229
$Mn^1(CO)_2(\eta^5\text{-cp}).$ $(\eta^2\text{-}CH_2\text{=}CHCOCH_3)$	or	$P2_12_12_1$	4	771.8(2) 1040.2(5) 1372.3(4)	 	MnC_9	OC 178.7(7,1) (cp)C 213.7(8,28) (η^2)C 216.2(8,13)	88.8(4) o	230

Table 11, cont. (6)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$Mn(CO)_2(\eta^5\text{-cp})$. [f] $(\eta^2\text{-}CH_2\text{=}CPh(OCOMe)$	m	$P2_1/a$	8	2238(2) 1483(1) 912(1)	 91.60(8) 	MnC_3 MnC_3	OC 178(2,3) (cp)C 219(2,0) (η^2)C 217(2,3) OC 175(2,3) (cp)C 217(2,1) (η^2)C 221(2,1)	89.6(8) f_1 91.3(8) f_2	231
$Mn(CO)_2(\eta^5\text{-cp})$. $\{\eta^2\text{-}C(Ph)_2\text{=}C\text{=}O\}$	m	$P2_1/c$	4	678(2) 1397(2) 1863(2)	 99.55 	MnC_3	OC 177(2,4) (cp)C not given (η^2)C 207(2,11)	not given	232
$Mn(CO)_2(\eta^5\text{-cp})(\eta^2\text{-}C_8H_8)$	m	$P2_1/c$	4	1081.3(7) 660.6(4) 1716.4(9)	 94.68(5) 	MnC_3	OC 178.7(2,4) (cp)C 215.6(2,15) (η^2)C 219.8(2,5)	88.8(1)	233
$Mn(CO)_2(\eta^5\text{-cp*})(\eta^2\text{-ak})$	tr	$\bar{P}1$	2	841.8(4) 1058.7(5) 1179.3(4)	107.59(3) 95.44(2) 112.18(3)	MnC_3	OC 179.9(7,30) (cp*)C 215.5 (η^2)C 210.9(6,133)	91.1(3)	234
$[Mn(CO)(\eta^5\text{-cp*})(\eta^3\text{-aac})$	m	$P2_1/c$	4	793.6(2) 1459.3(5) 1256.9(5)	 99.08(3) 	MnC_3	OC 168(1) (cp*)C 215(1,2) (η^3)C 204(1,15)	q	235
$Mn^1(CO)_3\{\eta^5\text{-}C_6H_6CH\text{-}$ $\text{-}[CO(OEt)]_2\}$	or	Pbcn	8	2524(1) 920(2) 1489(2)		MnC_3			236
$Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ [f]	m	$P2_1/c$	8	961.0(3) 2277.8(5) 1339.6(2)	 91.54(2) 	MnC_3 MnC_3	OC 179.9(6,13) C 220.8(5,85) C 251.1(5) OC 179.7(7,9) C 219.0(6,81) C 250.5(5)	91.8(2,1.3) 91.9(2,2.4)	237
$Mn^1(CO)_3(\eta^6\text{-}C_{18}H_{24})]$. $.(BF_4)$	or	$P2_12_12_1$	4	995.0(2) 1039.8(2) 2041.2(3)		MnC_3	OC 179.5(11,14) C 221.2(8,18)	91.13(5,73) s	238

Table 11, cont. (7)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromo-phore	M-L [pm]	(O)C-M-C(O) (O)C-M-L [°]	Ref
$Mn(CO)_2(\eta^6\text{-}C_6Me_6)Cl^r$	m	$P2_1/c$	4	870.1(3) 1361.8(5) 1326.6(4)	 120.82(1) 	MnC_8Cl	OC 220.70(26,448) C 185.3(4,10) Cl 235.43(10)	89.37(11) 89.85(9,34)	239
$Mn(CO)_3(\eta^6\text{-}PhB)$	or	Pbca	8	1047(1) 1554(2) 1636(2)	 	MnC_8B	OC 179.7(8,4) C 220.1(7,46) B 238.5(8)	91.1(3,1.9)	240

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c (cp)C-Mn-C(cp) = 38.14(8,67)°.
d (η^5)C-Mn-C(η^5) = 37.6(4,1.3) and 79.5(5,9.5)°.
e (η^5)C-Mn-C(η^5 = 38.7(3,5)°.
f There are two crystallographically independent molecules.
g (O)C-Mn-C(cp) = 88.64(9) - 154.39(9)°; C-Mn-C(cp) = 96.89(9) - 159.00(9)°; (cp)C-Mn-C(cp) = 37.72(10,36) and 63.07(9,20)°.
h At 153K.
i P-Mn-C(O) = 90.73(9)°; P-Mn-C(cp) = 87.60(9) - 147.14(9)°; and P-Mn-C = 94.88(7)°.
j (O)C-Mn-N = 102.8(3)°; (O)C-Mn-P = 102.2(2)°; and N-Mn-P = 93.9(2)°.
k (O)C-Mn-I = 91.0(2)°; Mn-C(centroid of cp*) = 179.4 pm.
l (η^1)C-Mn-N = 98.9(-,1.0)°; N-Mn-N = 78.6°; N-Mn-C(centroid of η^5-cp) = 117.4(-,6)°.
m At 170K; (O)C-Mn-C(cp) = 124.1(5)°; (O)C-Mn-C(C_7H_8) = 108.5(1)°; (cp)C-Mn-C(C_7H_8) = 117.4(5)° (C_7H_8)C-Mn-C(C_7H_8) = 38.0(1)°; Mn-C(centroid of cp) = 177.3(3) pm.
n_1 (O)C-Mn-C(centroid of cp) = 120.1(3,2.2)°.
n_2 (O)C-Mn0C(centroid of cp) = 120.8(2,2.4)°.
o (O)C-Mn-C(dep) = 77.8(4) and 88.8(4)°; (O)C-Mn-C(centroid of cp) = 92.3(4) and 100.6(4)°, (dep)C-Mn-C(dep) = 37.5(3)°.
p (O)C-Mn-C(centroid of cp) = 122(-,2)°; (O)C-Mn-C(centroid of n^2) = 93(-,3)°; (centroid of cp)C-Mn-C(centroid of n^2) = 127°.
p (O)C-Mn-C(centroid of cp) = 122(-,2)°; (O)C-Mn-C(centroid of n^2) = 93(-,3)°; (centroid of cp)C-Mn-C(centroid of n^2) = 128°.
q (O)C-Mn-C(aac) = 86.2(4,1.4) and 103.7(4)°; and (aac)C-Mn-C(aac) = 37.7(3), 79.4(4) and 111.8(4)°.
r At 115K.
s C-Mn-C = 37.32(3,88), 67.32(3,42) and 79.60(3,50)°.

mean Mn-C(CO) bond distance is smaller in the former (179.2 to 179.9 pm) while the Mn-C(multidentate) distance is bigger (220.4 to 210.8 pm).

There are four examples [185-188] in which the manganese atoms are surrounded by eight donor atoms with the chromophores: MnC_7H [185]; MnC_7N [186]; MnC_7P [187]; and MnC_7As [188]. In each case the chromophores are built up from three carbonyl groups and one pentadentate heterocyclic ligand. The mean Mn-C and Mn-X distances increase with the size of the pentadentate ligand and the radius of X: 215.4(3) and 186(2) pm (H,37 pm) [185] <216 and 216 pm (N,75 pm) [186] <215.9(8) and 237.9(2) pm (P,110 pm) [187] <219.3(5) and 249.2(2) pm (As,122 pm), respectively.

3. Compounds with penta- or hexadentate carbon ligands

Crystallographic and structural data for this class of compound are listed in Table 11, from which it may be seen that the most common ligands are carbonyl and cyclopentadienyl. The molecular structure of the monoclinic $Mn(CO)_2(\eta^5\text{-cp})(CPh_2)$ [203] is shown in Figure 14 as a example. The manganese atom is located directly below the centre of the cyclopentadienyl ring at an average 217.2 pm away from each carbon. The two carbonyl ligands are linear (Mn-C-O = 178.0) and have normal Mn-C (178.8 pm and C-O (114.8 pm) bond distances. The carbene ligand has a Mn-C(8) distance of 188.5(2) pm.

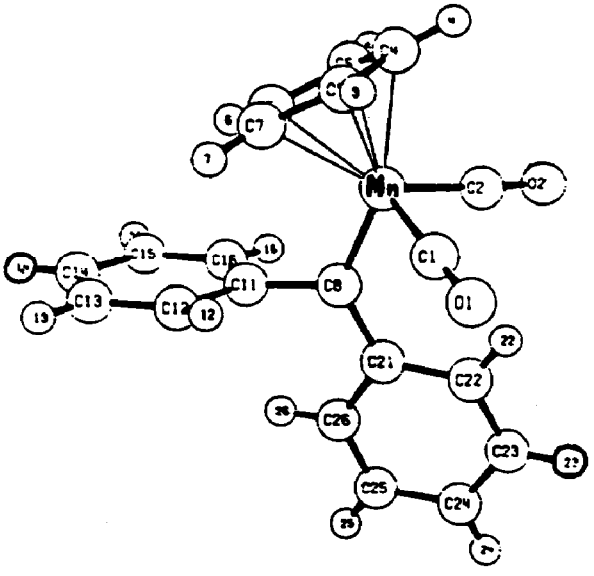

Figure 14. Structure of $Mn(CO)_2(\eta^5\text{-cp})(CPh_2)$
Reproduced with permission from J. Amer. Chem. Soc. [253]

Table 12 Crystallographic and structural data for manganese compounds with two multidentate ring ligands[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	C^c-Mn-L C^c-Mn-C^c [°]	Ref
$Mn^0(\eta^4\text{-}C_4H_8)_2(CO)$	tg	$P42_1m$	2	780(1) 780(1) 721(1)	90 90 90	MnC_8	$(\eta^4)C^b$ 211(1,5) OC 184(1)	not given	241
$Mn^0(\eta^4\text{-}C_8H_8)_2(CO)$	or	$P2_12_12_1$	4	857.0(1) 1722.0(1) 756.2(1)		MnC_9	$(\eta^4)C$ 211.9(7,46) OC 179.1(6)	89.5(3,1.9)	242
$Mn^0(\eta^4\text{-}C_4H_8)_2\{P(OMe)_3\}^d$	m	$P2_1/c$	4	1413.7(2) 784.1(1) 1201.7(2)	 97.73(1) 	MnC_8P	$(\eta^4)C$ 210.3(3,38) P 218.8(1)		243
$Mn(\eta^8\text{-tmdt})(PMe_3)$	m	$P2_1/c$	4	801.7(2) 1477.1(4) 1587.8(4)	 113.32(3) 	MnC_8P	$(\eta^8)C$ 211.1(4,58) P 229.0(1)	90.7(1,3.2),126.1(1,2.3)	244
$Mn^{II}(\eta^5\text{-cp})_2^e$						MnC_{10}	C 238.0(6)		245
$Mn^{II}(\eta^5\text{-cp})_2^f$	or	$Pna2_1$ (Pnam)	4	1402.7(2) 582.9(1) 996.5(1)		MnC_{10}	C 247		246
$Mn^{II}(\eta^5\text{-}C_5H_4CH_3)_2^{g_1}$						MnC_{10}	C 243.3(8)^{g_2}		247
						MnC_{10}	C 214.4(12)^{g_3}		
$Mn^{II}(\eta^5\text{-}C_5Me_5)_2^h$						MnC_{10}	C 213.0(4)		
$Mn^{II}(\eta^5\text{-}C_5Me_5)_2$	m	C2/c	4	1514.3(4) 1224.8(3) 991.0(3)	 93.56(3) 	MnC_{10}	C 211.4(2,9)	39.22(7,52) 65.79(7,35) 114.21(7,35) 140.78(7,52)	249
$Mn(\eta^5\text{-}C_5H_4CH_3)$. $(\eta^6\text{-}C_{13}H_{12})$	m	$P2_1/c$	4	754(1) 1177(2) 16.42(2)	 80.6(2) 	MnC_{11}	$(\eta^5)C$ 212(2,2) $(\eta^6)C$ 210(2,5)	38-169	250

Table 12, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	C^C-Mn-L_C C^C-Mn-C^C [°]	Ref
$Mn^{II}\{(\eta^5\text{-cp})_2pr\}(C_5H_3NCl_2)$						$MnC_{10}N$	(η^5)C 240.2-248.3(7) N 231.0(6)	j	251
$Mn^{I}(\eta^5\text{-cp})(\eta^6\text{-}C_{23}H_{17}P)$[i]	tr	P$\bar{1}$	4	1584.3(5) 1366.5(3) 1015.5(2)	93.89(3) 102.75(3) 89.00(3)	$MnC_{10}P$	(η^5)C 211.7(5,20) C 215.5(5,108) P 234.6(2)	not given	252
						$MnC_{10}P$	(η^5)C 209.2(6,9) C 210.9(6,14) P 237.6(2)		
$Mn^{II}(\eta^5\text{-cp})_2(PMe_3)$	m	$P2_1/c$	4	824.3(1) 1530.3(1) 1147.6(2)	108.04(1)	$MnC_{10}P$	(η^5)C 252.3(7,107) P 257.7(4)	k_1	253
$Mn^{II}(\eta^5\text{-cp})_2(PMePh_2)$	m	$P2_1/c$	4	908.0(1) 1016.1(1) 2176.9(1)	100.66(1)	$MnC_{10}P$	(η^5)C 251.4(7,210) P 261.3(4)	k_2	253
$Mn^{II}(\eta^5\text{-cp})_2(dmpe)$	tg	P4n2	4	1389.2(2) 1389.2(2) 905.0(3)		$MnC_{10}P_2$	(η^5)C 261.4(8,128) P 267.4(4,0)	k_3	253

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c Multidentate ligand.
d At 173K
e By gas phase electron diffraction at about 413K.
f Polymeric structure.
g_1 By gas phase electron diffraction at about 373K. g_2 High-spin species. g_3 Low-spin species.
h By gas phase electron diffraction at about 443K.
i There are two crystallographically independent molecules.
j (centroid)cp-Mn-cp(centroid) = 140(2)°.
k_1 (centroid)cp-Mn-cp(centroid) = 142.3(4)°; (centroid)cp-Mn-P = 108.8(2,8)°.
k_2 (centroid)cp-Mn-cp(centroid) = 142.2(2)°; (centroid)cp-Mn-P = 108.6(5,1.9)°.
k_3 (centroid)cp-Mn-cp(centroid) = 136.9(2)°; (centroid)cp-Mn-P = 105.6(2); P-Mn-P = 77.4(2)°.

The data can be separated into three crystal classes, the most common being monoclinic followed by orthorhombic and then triclinic. Two crystallographically independent molecules have been found in several cases [199,200,-229,231,237] as examples of distortion isomerism.

The mean Mn-C(CO) and Mn-C(cp) bond distances increase with the coordination number in the order eight <nine, corresponding to the values 178.0 and 215.0 pm <180.5 and 215.6 pm respectively.

In the series of manganese eight coordinate compounds the mean Mn-C bond distance increases with the ligand size in the order: 178.0 pm (CO) <187.0 pm (other unidentate C-ligand) <215.0 pm (pentadentate). For the nine-coordinate derivatives the order is: 180.4 pm (CO) <213.9 pm (bidentate-C) <215.6 pm (pentadentate). In addition the mean Mn-P distance decreases from 225.1 pm (PPh_3) to 217.4 pm ($P(OMe)_3$), reflecting the decrease in steric demand of the phosphine ligand.

4. Compounds with two multidentate ring ligands

Crystallographic and structural data for these derivatives are summarized in Table 12. The cyclopentadienyl radical is again one of the most commonly found π-donor ligands. The data is arranged in increasing order of coordination number and increasing order of atomic number of the principal coordinating ligand. The compounds can be classified into two groups, those with a parallel ring "sandwich" arrangement and those with an open or "clino-sandwich" arrangement. There are five examples of the former, including those with two cyclopentadienyl rings, and those with cyclopentadienyl and cycloheptatrienyl rings [250]. While the electronic ground-state of $Mn(cp)_2$ [245,246] is high spin, that of decamethylmanganocene is low spin.

Electron diffraction studies of 1,1-dimethylmanganocene [247] shows that the gas contains two geometrically distinct species of high and low spin respectively. The larger Mn-C vibrational amplitude of 16.0(16) pm of the low spin species compared to that of 11.11(8) pm for the high spin species is consistent with the existence of a dynamic Jahn-Teller effect involving the ring tilting modes [247].

It is noted that the mean Mn-C bond distance 212.7 pm (range 211.4-214.4 pm) found in the low-spin manganese(11) compounds is far shorter than 242.8 pm (range 238.0-247.0 pm) found in the high spin ones. The relatively long distances in the high-spin manganese(11) derivatives are related to the singly occupied $d_{x^2-y^2}$ orbital.

The remaining examples in Table 12 are of the "clino-sandwich" structural type. The structure of high-spin $Mn(\eta^5\text{-cp})_2$ (dmpe) [253] is shown in Figure 15 as an example. The compound has crystallographic C2 symmetry and a pseudo tetrahedral geometry, if the cyclopentadienyl ring is regarded as occupying one coordination site. The Mn-C distances are 249.2(6) to 274.2(8) pm with an

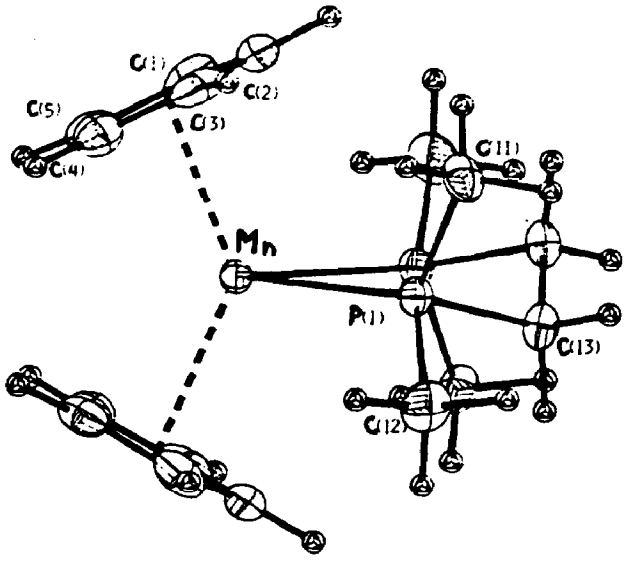

Figure 15. Structure of $Mn(\eta^5\text{-cp})_2$(dmpe)
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average value of 261.4 pm, and the Mn-P distance is 267.4(4) pm. The presence of the ligand dmpe causes the (centroid)cp-Mn-cp(centroid) angle to decrease to 136.9(2)°. As the steric demand of this extra ligand decreases, so does the Mn-P distance to 261.3 pm in $Mncp_2(PMePh_2)$ and to 257.7 pm in $Mncp_2(PMe_3)$ [253].

There are examples in which the manganese atom is η^4-bonded to two rings with one additional unidentate ligand [241-244]. The manganese adopts a square pyramidal configuration with the unidentate ligand in the apical position.

The mean Mn-C(cp) distance of 242.8 pm found for the high-spin sandwich manganese(11) compounds is about 9.6 pm shorter than for these "clino-sandwich" derivatives (252.4 pm). Two crystallographically independent molecules have been found for $Mn(\eta^5\text{-cp})(\eta^6\text{-}C_{23}H_{17}P)$ [252] which differ mostly by degree of distortion.

(B) Binuclear manganese organometallic compounds

Table 13 lists the available data for these compounds in the order of increasing Mn-Mn distance. The data can be subdivided into several bridge types. The crystal structure of green monoclinic $Mn_2(\mu\text{-CO})_3(\eta^5\text{-}C_5Me_5)_2$ [254] is shown in Figure 16. The three bridging carbonyl groups bring the manganese

Table 13 Crystallographic and structural data for binuclear manganese organometallics[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
$Mn_2(\mu\text{-}CO)_3(\eta^5\text{-}C_5Me_5)_2$	m	$P2_1/c$	4	972.3(6) 1426.7(2) 1674.7(2)	 106.1(2) 	MnC_8	$(\eta^5)C_d$ 192.9(5) OC_d 214.7(5)	217.0(1) 177.6(5) 6850(2)	91.4(2)	254
$Mn_2\{\mu\text{-}NN(SiMe_3)_2\}_2(\eta^5\text{-}cp)_2$	m	$p2_1/c$		1326.6 814.7 1538.4	 108.54 	MnC_5N_2	C_d 213.6(9) N^d 178.5(8,3)	239.3(2) e 84.2(3)	84.2(3)	255
$Mn_2(\mu\text{-}NO)_2(NO)(\eta^5\text{-}cp)_2.$ $.(\eta^1\text{-}cp)$	or	Pnma	4	1820.1(3) 1080.2(2) 787.7(2)		$Mn^{II}C_5N_3$ $Mn^0C_6N_2$	ON 165.6(5) $(\eta^5)C_d$ 215.8 ON 194.4(3) $(\eta^1)C$ 216.1(4) $(\eta^5)C_d$ 215.8(5) ON 175.2(3)	252.0(1) e e	e	256
$Mn_2(\mu\text{-}NO)_2(NO)(NO_2).$ $.(\eta^5\text{-}cp)_2$	m	$P2_1/c$	4	701.3(3) 1245.3(1) 1624.6(10)	 110.00(6) 	$Mn^{II}C_5N_3$ $Mn^0C_5N_3$	O_2N 199.2(10) $(\eta^5)C_d$ e ON 177.5(10) ON 165.2(10) $(\eta^5)C_d$ e ON 194.3(10)	252.6(10) e e	e	257
trans-$[Mn(CO)(NO)(\eta^5\text{-}cp)]_2$	m	$p2_1/c$	2	700.2(1) 1249.1(3) 802.3(2)	 108.07(1) 	$MnC_5X^f_3$	X 172.3(4) $(\eta^5)C_d$ 213.1(5,20) X^d 190.6(4,5)	257.1(1) 180.0(6) 84.8(1)	95.5(2,5)	258
$Mn_2(CO)_5(\mu\text{-}CO)(\mu_2\text{-t-bu-iae})$	or	$P2_12_12_1$	4	1687.8(7) 1939.4(9) 908.4(3)		MnC_4N_2 MnC_3N_3	OC_d 179(2) OC_d 234(2) N^d 204(1,1) OC_d 179(2) OC_d 181(2) N^d 209(1,7)	258.5(6) - e	e	259

Table 13, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
$Mn_2(\mu_2\text{-tmi})(CO)_6$	tr	$P\bar{1}$	2	735.2(2) 886.3(2) 1232.4(6)	83.44(4) 85.66(3) 72.45(2)	MnC_5N_2	OC 180.4(4,4) C_d 214.2(4,5) N^d 211.0(3,2)	261.5(1) - 79.3(1,2)	90.9(2,3.1) g_1	260
						MnC_3N_2	OC 180.1(4,12) N^d 198.6(3,9)		89.2(2,3.4) g_2	
$Mn_2(\mu_2\text{-hdd})(CO)_7$	tr	$P\bar{1}$	2	907.6(3) 917.2(4) 905.5(3)	90.49(3) 103.63(3) 96.10(3)	MnC_6	OC e C^d 207.3(1,2)	265.4(1) - e	79.2(1) 96.3(1)	261
						MnC_7	OC e C_d 212.5(1,9) C^d 212.9(1,3)		e	
$Mn_2(\mu\text{-}CH_2Ph)_2(CH_2Ph)_2\cdot(PMe_3)_2$	m	$P2_1/c$	2	1209.6(2) 1008.9(3) 1514.4(3)	112.63(3)	MnC_3P	C_d 212.7(3) C^d 231.4(3,78) P 256.2(1)	266.7(1) - 70.3(2)	h	262
$Mn_2(\mu\text{-CO})(\mu\text{-}C_3H_4)(CO)_2\cdot(\eta^5\text{-cp})_2$	m	$P2_1/c$	4	1325.3(5) 1576.8(7) 737.6(3)	115.80(4)	MnC_8	OC 177.5(5,1) C 217.3(5,5) $(\eta^5)C_d$ 214.1(5,29) C_d 197.6(5,1) OC^d 197.2(5,11)	269.1(2) e 86.0(2,1)	i	263
$Mn_2(\mu\text{-}CH_2CMe_3)_2(CH_2\cdot CMe_3)_2(PMe_3)_2$	or	$Pna2_1$	4	2067.2(5) 934.5(5) 1786.8(2)		MnC_6	C_d 217(3,3) C^d 236(2,13) P 267(1,0)	271.8(3) - 70.3(6,7)	j	262
$\{Mn(CO)_2(\eta^5\text{-cp})\}_2\cdot\mu\text{-}C{=}CHPh)$	or	$P2_12_12_1$	4	1533.6(3) 1539.1(3) 799.8(1)		MnC_8	OC 175(1,1) $(\eta^5)C_d$ e C^d 197(1,3)	273.4(2) e 88.0(5)	e	206
$[Mn_2\{\mu\text{-}C(CO)C_6H_4Me\text{-}p\}\cdot(CO)_6(\eta^5\text{-cp})]O.5Et_2O$	tr	$P\bar{1}$	2	818.9(3) 1807.7(9) 763.8(4)	95.66(4) 106.30(3) 85.47(3)	MnC_5	OC e C^d 212.8(4)	273.5(1)	e	264
						MnC_8	OC e $(\eta^5)C_d$ e C^d 212.8(4)			

Table 13, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
$Mn^{II}_2(\mu\text{-}CH_2SiMe_3)_2(CH_2Si.Me_3)_2$	tr	$P\bar{1}$	1	1031.1(1) 1061.0(2) 1096.3(2)	67.14(1) 86.92(1) 61.52(1)	MnC_3P	C_d 211.1(3) C 228.9(4,81) P 265.0(1)	277.2(1) - 74.5(1)	e	266
$\{Mn(CO)_2(\eta^5\text{-}cp^*)\}_2(\mu\text{-}CH_2)$	tr	$P\bar{1}$	2	683.4(6) 960.2(2) 1360.5(5)	108.29(2) 92.95(5) 104.85(4)	MnC_8	OC 178.5(5,16) $(\eta^5)C$ 215.5(8,16) C^o 201.4(5,1)	277.9(1) 177.,8 87.3(2)	85.9(2,1)	267
$\{Mn(CO)_2(\eta^5\text{-}cp)\}_2(\mu\text{-}CH_2)^{[1]}$	or	Pccn	4	716.1(4) 1517.7(6) 1270.3(6)		MnC_8	OC 178.5(2,7) $(\eta^5)C$ 216.3(2,13) C^d 202.6(2,0)	279.96(11) 179.4 87.40(7)	86.39(8) l_1	268
				$727.5(6)^{\frac{1}{2}}$ 1536.7(8) 1283.5(8)						
$Mn^{II}_2(CH_2C_6H_4NMe_2)_4$	m	Cc	8	2192.0(40) 2318.6(14) 1398.8(6)	107.77(8)	MnC_3N_2	C 218 N_d 241(-,1) C^d 235(-,4)	281.0(3) - 74.4	m	269
						MnC_3N	C 214 N 230 C^d 230(-,0)			
$Mn_2(\mu\text{-}CH_2SiMe_3)_2(CH_2Si.Me_3)_2(PMePh_2)_2$	m	$P2_1/c$	2	1155.1(1) 1082.9(5) 2096.4(3)	104.52(1)	MnC_3P	C_d 211.7(5) C^d 229.1(5,98) P 268.4(1)	282.8(1) - 76.1(4)	n	262
$[Mn_2(CO)_4\{\mu\text{-}C(O)CH_2N_2\}.(pi\text{-}dppmm)_2]2CH_2Cl_2$	tr	$P\bar{1}$	2	1254.9(6) 1344.7(2) 1914.0(6)	104.34(2) 95.99(3) 111.11(2)	MnC_3P_2N	OC 180.4(10,23) C 200.1(9) P_d 229.5(2,0) N^d 196.7(7)	289.8(2) - 97.3(3)	o_1	270
						MnC_2P_2N	OC 178.7(11,23) P_d 229.1(2,4) N^d 189.4(7)		o_2	

Table 13, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
$Mn_2(\mu\text{-}AsMe_2)(CO)_6(\eta^5\text{-}cp)$	or	Pbca	4	1115.7(8) 1266.5(8) 2250.7(14)		MnC_7As	OC 178(2,5) $(\eta^5)C_d$ 217(3,6) As^d 236.2(4)	291.2(4) e 76.3(1)	p_1	271
						MnC_4As	OC_d 181(2,5) As^d 235.0(4)		p_2	
$[\{Mn(CO)_2(\eta^5\text{-}cp^*)\}_2.$ $.(\mu\text{-}SEt)](ClO_4)$	m	$P2_1/n$	4	867.6(5) 1606.2(5) 1587.2(5)	104.45(20)	MnC_7S	OC 181.5(9,15) $(\eta^5)C_d$ 215.9(7,80) S^d 225.6(2,14)	293.0(1) e 81.0(1)	84.5(3,5) q	272
$Mn_2^0(CO)_6(\eta^8\text{-}C_8H_8)$	or	Pbca	8	1009.6(3) 2382.5(8) 1147.2(4)		MnC_7	OC 179.0(14,11) $(\eta^8)C$ 219.6(11,125)	304.5(2)	e -	273
$Mn^{II}_2(\mu\text{-}Cl)_2(\eta^5\text{-}cp^*)_2.$ $.(PEt_3)_2$	or	Pbca	8	1369(3) 1531.4(2) 1440.2(3)		MnC_5PCl	C e P_d 256.7(2) Cl^d 248.1(2,1)	351.4(2) 217.1(10) 90.2	e	274
$Mn_2(\mu\text{-}epb)CO)_6$	or	Pbca	8	1429(1) 1670(1) 1541(1)		MnC_7B	OC_d 178(1,2) C_d 216(1,6) B^d 225(1,1)	353.3(2)	90.0(6,2.4)	275
$[\{Mn(CO)_2(\eta^5\text{-}cp)\}_2.$ $.(\mu\text{-}CH_2CCH_2)]$						MnC_8	OC 176.9(6,10) $(\eta^5)C$ e C_d 211.9(6) C^d 214.6(3)	~380 e 131.3(4)	87.1(3)	276
$Mn_2(\mu\text{-}Cl)_2(CH_2SPh)_2(tmeda)_2$	tr	P1	1	840.3(2) 1140.1(4) 1156.9(4)	98.19(3) 110.69(2) 98.40(3)	MnN_2Cl_2C	C 217.7(9) N_d 228.4(10,50) Cl^d 255.6(3,145)	380.6(3) -	r	277
$Mn_2(\mu\text{-}\eta^5\text{-}C_4H_4N(CO)_6(acpr)$	m	$P2_1/c$	4	897.2(2) 831.7(1) 2446.7(5)	97.38(2)	MnC_7N	OC 179.0(5,7) C_d 214.4(5,8) N^d 212.0(4)	384.0(1) e e	e	278

Table 13, cont. (5)

Table 13, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
						MnC_3N_2O	OC 179.5(5,19) N 202.2(4) O[d] 206.6(3) N[d] 210.4(4)			278
$[\{Mn^I(CO)_3\}_2(\mu\text{-}AsMe_2).(\mu\text{-}As_2Me_4F_8C_4)]$	tr	P1	2	958.0(4) 1527.9(6) 929.2(3)		MnC_3As_3	OC 174(3,4) As[d] 237.1(4,17) Me_2As[d] 245.5(4)	410.8 - 111.8(1)	93.4(10,8) s_1	279
						MnC_6As	OC 179(3,1) C[d] 210(2,3) Me_2As[d] 250.7(4)		92.0(11,6.0) s_2	
$[\{Mn(CO)_4\}_2(\mu\text{-}AsMe_2).(\mu\text{-}AsMe_2F_4C_4)]$	m	$P2_1/n$	4	904.0(3) 1355.2(4) 1851.7(5)	90.52(2)	MnC_5As	OC 183.3(9,23) C[d] 202.7(7) Me_2As[d] 248.9(2)	447.5 - 127.15(5)	92.4(4,1.7) 172.4(4) t_1	280
						MnC_4As_2	OC 182.7(9,25) As[d] 241.0(2) Me_2As[d] 250.8(2)		92.2(4,2.3) 172.1(4) t_2	
$[\{Mn(CO)_2(\eta^5\text{-}cp)\}_2.(\mu\text{-}PC_6H_5)]$						MnC_7P	OC e $(\eta^5)C$[d] P[d] 218.4(2,5)	e e 138(1)	e e	281
$[\{Mn(CO)_3\}_2(\mu\text{-}B(Ph).C_4H_3(Et)]$	or	Pbca	8	1429(1) 1670(1) 1541(1)		MnC_7B	OC[d] 178 C[d] 215 B[d] 224			282
$[\{Mn(CO)_2(\eta^5\text{-}cp^*)\}_2(\mu\text{-}N_2)]$	m	$P2_1/n$	2	800.4(2) 1034.4(3) 1013.5(3)	97.69(4)	MnC_7N	OC 178.0(7,2) $(\eta^5)C$[d] 214.5(7,32) N[d] 187.5(5)	e -	90.5(3) u	283
$[\{Mn(CO)_2(\eta^5\text{-}cp)\}_2(\mu\text{-}S_2)]$	m	$P2_1/c$	2	951.8(7) 702.7(5) 1181.6(8)	99.56(5)	MnC_7S	OC 179(2,0) $(\eta^5)C$[d] 219(3,9) S[d] 216.7(4)	- e	89.1(8) v	284

Table 13, cont. (6)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
[{Mn(CO)$_2$(η^5-cp)}$_2$(μ-P(H).(Ph)P(H)(Ph)]	m	$P2_1/c$	2	1095(1) 1145(1) 1186(1)	 124.73(5)	MnC_7P	OC 178.5(9,3) (η^5)C[d] 213(1,2) P 221.6(3)	 e	93.4(4) x	285
[{Mn(CO)$_2$(η^5-cp)}$_2$(μ-As(H).(Ph)As(H)(Ph)]	m	$P2_1/c$	2	1058(1) 1148(1) 1200(1)	 120.85(8)	MnC_7As	OC 178(1,1) (η^5)C[d] 211(1,4) As 231.9(3)	 e -	93.8(5) y	286
$Mn_2(CO)_7(PPh_3)\{(CO)C_6H_3.PPh_2\}$	m	$P2_1/c$	4	1118.5(2) 2692.2(4) 1460.6(3)	 115.90(1)	MnC_4PO	OC 176.1(15,65) C 204.1(12) P 236.4(4) O 206.4(8)	 - -	91.7(7,2.6) z_1	287
						MnC_5P	OC 179.8(17,26) C 201.6(12) P 230.4(4)	 - -	92.2(7,3.0) 172.6(6) z_2	
$Mn_2(CO)_6(PPh_3)_2\{(CO)C_6H_3.PPh_2\}$	tr	P1	2	1084.7(2) 1378.2(3) 1937.0(4)	97.79(2) 96.77(2) 103.03(2)	MnC_4PO	OC 175.8(27,20) C 200.1(21) P 236.7(7) O 209.4(13)	 - -	88.8(11,1.1) z_3	287
						MnC_4P_2	OC 178.4(25,41) C 205.8(21) P 229.8(8,24)	 - -	92.3(10,4.0) 168.1(10) z_4	
$Mn_2(CO)_7(PPh_3)\{(CO)C_6H_3.PPh_2\}$	m	C2/c	8	1076.3(2) 3471.3(5) 2147.9(3)	 92.93(1)	MnC_5O	OC 183.2(10,27) C 204.5(7) O 205.3(5)	 - -	91.6(4,3.3) 175.9(4) z_5	288
						MnC_4P_2	OC 183.3(9,15) C 204.0(7) P 230.7(2,31)	 - -	93.4(3,4.8) 173.1(3) z_6	
$Mn_2(CO)_6\{\eta^5\text{-}C_4H_4N(pcr)\}^{Z_7}$	tr	P1	4	1937.79(5) 1672.3(6) 680.0(3)	85.29(3) 83.66(3)	MnC_7N	OC 178(1,3) (η^5)C 213(1,2) N 210(1)	 - -	91.5(7,1)	289

Table 13, cont. (7)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromo-phore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
						MnC_3O_2N	OC 178(1,1)		89.5(6,6)	289
							N 209(1)	-	z_8	
							O 200.5(9,16)	-		
						MnC_7N	OC 175(2,2)		90.5(8,2.3)	
							(η^5)C 213(2,2)	-		
							N 212(1)	-		
						MnC_3O_2N	OC 180(1,1)		88.1(7,2.4)	
							N 210(1)	-	z_9	
							O 202.3(9,35)	-		
[{$Mn^I(CO)_2(\eta^5$-cp)}$_2$-{(μ-PMe_2)$_2$O}]	m	$P2_1/c$	2	1115.6(6) 841.9(6) 1469.9(18)	130.9(1)	MnC_7P	OC 175.7(5,6)		90.8(3)	290
							(η^5)C e	-	z_{10}	
							P 217.8(1)	-		
[{$Mn^I(CO)_2(\eta^5$-cp)}$_2$-{(μ-PMe_2)$_2$S}]	or	Iba2	8	1665(1) 1569(1) 1749(1)		MnC_7P	OC 176(1,2)		91.7(6,1.7)	291
							(η^5)C e	-	z_{12}	
							P 218(1,1)	-		
						MnC_7P	OC 175(2,3)		90.4(9,2.0)	
							(η^5)C e	-	z_{13}	
							P 219(1,1)	-		
[$Mn(CO)_3(\eta^5$-$C_{10}H_8$)]$_2$	m	$P2_1/c$	4	1448.2(1) 1041.6(2) 1489.6(2)	93.56(1)	MnC_8	OC 179.31(26,65)		92.01(12,3.03)	292
							(η^5) 215.06(24,404)	-		
[$Mn(CO)(NO)(\eta^5$-cp).$(CONH_2)$]$_2$	m	$P2_1/n$	4	822.8(5) 918.5(6) 1165.7(6)	99.23(5)	MnC_7N	OC 178.3(6,12)		z_{14}	293
							(η^5)C 214.4(5,15)	-		
							ON 166.3(5,12)	-		
							H_2NOC 202.6			
[{$Mn(CO)_2(\eta^5$-cp)}$_2$.(μ-η^4-C_5H_6)]	m	$P2_1/c$	4	1226(1) 1144(1) 1231(1)	102.30(8)	MnC_8	OC 176.9(9,13)		89.5(4,1.5)	294
							(η^5)C 214.3(9,29)	-		
							(η^4)C 221.1(8,35)	-		

Table 13, cont. (8)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromo-phore	M-L [pm]	M-M(pm) M-CNT[b](pm) M-L-M [°]	L-M-L [°]	Ref
$Mn_2(CO)_8(\mu\text{-}\eta^{10}\text{-}C_{14}H_8Me_2)$	or	$P2_12_12_1$	4	967.77(14) 1309.99(20) 1563.85(26)		MnC_8	OC 178.4(17,48) C 218.8(14,216)	-	92.9(7,6.7)	295
$Mn_2(CO)_5(\eta^5\text{-cp}).\text{-}$ $\{\mu\text{-}SC(Ph)C_5H_4\}$	tr	P1	2	1000.7(3) 1000.9(3) 1172.9(3)	92.26(3) 109.19(3) 112.56(3)	MnC_7S MnC_8	OC 179.1(7,1) (η^5)C 214.5(8,12) S 219.3(2) OC 180.1(7,7) C 213.9(7,14)	- -	92.3(3,2.6) z_{15}	296
$[\{Mn(CO)_2(\eta^5\text{-cp}^*)\}_2.$ $(\mu_2\text{-cbdcp})]$	m	$P2_1/n$	2	1123.9(7) 1107.4(3) 897.5(4)	93.49(6)	MnC_8	OC 176.2(12,3) (η^5)C 216.4(12,34) C 187.8(8)	- -	89.6(4,3.3)	297
$Mn_2(CO)_8(\mu\text{-bcpf})$	tr	P1	2	1025.9(7) 1084.8(8) 1468.5(10)	98.47(6) 92.03(5) 98.99(6)	MnC_8	OC 179.2(4,10) C 213.9(4,20)	-	92.9(2,1.1)	298
$Mn_2(CO)_8(\mu\text{-bcpp})$	m	C2/c	4	2450.9(2) 2955.40(5) 2081.2(2)	90 141.502(4) 90	MnC_8	OC 179.5(6,13) C 214.8(7,25)	-	92.6(3,2.4)	298

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b CNT, centroid of the multidentate ring ligand.
c The chemical identity of coordinated atom or ligand.
d The bridge atom (ligand).
e Not given.
f X labelled the disordered C and N atoms.
g_1 The value of (O)C-Mn-C(O) angle; (O)C-Mn-C = 94.2(2) - 146.1(2)°; (O)C-Mn-N = 96.4(2) - 160.8(2)°; C-Mn-C = 38.3(1)°; C-Mn-N = 38.4(1,2) and 66.3(1,0)°; and N-Mn-N = 71.7(1)°.
g_2 The value of (O)C-Mn-C(O) angle; (O)C-Mn-N = 96.4(2) - 163.4(2)°; and N-Mn-N = 76.9(1)°.
h C-Mn-C^d = 110.7(2,2.1)°; C-Mn-P = 119.2(2)°; C^d-Mn-C^d = 109.7(2)°, and C^d-Mn-P = 90.4(2) and 113.5(2)°.
i Mn-Mn-Mn = 134.49(-,6)°; (O)C-Mn-C(O)^d = 84.5(2,1)°; C^d-Mn-C(O) = 80.0(2,9)°; C^d-Mn-C(O)^d = 94.0(2,3)°; C-Mn-C^d = 38.9(2,2)°; C-Mn-CNT = 93.54(-,34)°.
j C-Mn-C^d = 110.612(1,1.506)°; C-Mn-P = 123.123(1)°; C^d-Mn-C^d = 111.108(1)°; and C^d-Mn-P = 85.86(1) and 114.115(1)°.

Table 13 footnotes, continued

k At 143K. Mn-Mn-Mn = 129.0(-,1.3)°'(O)C-Mn-C(O) = 89.0(3,1.0)°; (O)C-Mn-C = 78.1(3,8) and 115.3(3,1.1)°.
l_1 At 130K; (O)C-Mn-C^a = 77.65(6) and 113.82(6)°.
l_2 At room temperature.
m C^a-Mn-C^a = 105.6°.
n C-Mn-C^a = 113.7(3) and 122.4(3)°; C-Mn-P = 107.4(4)°; C^a-Mn-C^a = 103.9(2)°; and C^a-Mn-P = 103.8(3,1.0)°.
o_1 (O)C-Mn-C(O) = 90.2(4)°; (O)C-Mn-P = 89.5(3,1.2)°; (O)C-Mn-N = 98.8(4) and 171.0(4)°; N-Mn-P = 89.9(2.2)°, and P-Mn-P = 177.3(1)°.
o_2 (O)C-Mn-C(O) = 94.1(4)°; (O)C-Mn-C = 86.1(4) and 179.8(1)°; (O)C-Mn-N = 100.0(3) and 165.9(3)°; (O)C-Mn-P = 91.0(3,3.0)°; C-Mn-N = 79.9(3)°; C-Mn-P = 86.8(2,4)°; N-Mn-P = 90.5(2,1); and P-Mn-P = 173.1(1)°.
p_1 (O)C-Mn-C(O) = 86.4(9)°; and (O)C-Mn-As = 88.0(6) and 109.4(6)°.
p_2 (O)C-Mn-C(O) = 92.9(9,2.8) and 172.6(9)°.
q (O)C-Mn-S = 86.2(2,3.4) and 115.4(2,1.8)°.
r N-Mn-N = 79.0(3)°; Cl-Mn-Cl = 86.8(4,2.9)° and N-Mn-Cl = 110.0(4)°.
s_1 (O)C-Mn-As = 92.8(7,1.4) and 171.1(8,3)°; (O)C-Mn-As^a = 89.6(7,0) and 175.3(8)°; As-Mn-As = 81.3(1)°; and As-Mn-As^a = 83.6(1,8)°.
s_2 (O)C-Mn-C = 81.0(8) - 162.9(10)°; (O)C-Mn-As^a = 83.2(7,1.0) and 167.7(7)°; C-Mn-As^a = 86.5(5) - 109.8(5)°.
t_1 The values of cis- and trans- (O)C-Mn-C(O) angles; (O)C-Mn-C = 88.6(4,4.1) and 177.9(4)°; (O)C-Mn-As^a = 86.4(3,1.1) and 176.8(3)°; and C-Mn-As^a = 93.2(2)°.
t_2 The values of cis- and trans- (O)C-Mn-C(O) angles; (O)C-Mn-As = 89.0(3,8)and 179.1(10)°; (O)C-Mn-As^a = 87.0(3,3.7) and 177.6(3)°; and As-Mn-As^a = 90.91(5)°.
u (O)C-Mn-N = 96.1(3,2)°.
v (O)C-Mn-S = 94.0(6,6)°.
x (O)C-Mn-As = 93.0(3,6)°.
y (O)C-Mn-As = 92.6(3,1.0)°.
z_1 (O)C-Mn-C; C-Mn-P = 96.0(4)°; C-Mn-D = 79.4(4)° and P-Mn-O = 86.1(2)°.
z_2 The values of cis- and trans- (O)C-Mn-C(O) angles; (O)C-Mn-C = 87.2(7,6.0) and 174.5(6)°; (O)C-Mn-P = 91.3(5,2.0) and 171.,6(5)°; and C-Mn-P = 82.7(4)°.
z_3 (O)C-Mn-C = 89.1(10,3.1) and 175.4(10)°; (O)C-Mn-P = 92.3(9,1.0) and 177.2(8)°; (O)C-Mn-O = 95.4(9,5.6) and 171.4(9)°; C-Mn-P = 93.3(6)°; O-Mn-P = 87.4(4)° and O-Mn-C = 79.5(7)°.
z_4 (O)C-Mn-C = 88.2(9,7.8) and 171.9(10)°; (O)C-Mn-P = 90.4(8,2.4) and 176.9(3)°; and C-Mn-P = 82.7(7)°.
z_5 The values of cis- and trans- (O)C-Mn-C(O) angles; (O)C-Mn-C = 89.6(3,3.3) and 172.7(3)°; (O)C-Mn-O = 91.0(3,1.9) and 172.6(3)°; and C-Mn-O = 79.8(2)°.
z_6 (O)C-Mn-C = 87.9(3,7.0) and 170.7(3)°; (O)C-Mn-P = 90.6(2,5.1)°; C-Mn-P = 88.0(2,5.6)°; and P-Mn-P = 175.8(1)°.
z_7 At 153K, there are two crystallographically independent molecules.
z_8 (O)C-Mn-N = 92.0(5,2.1) and 176.9(5)°; (O)C-Mn-O = 91.9(5,2.2) and 177.0(5,1.1)°; O-Mn-N = 87.0(4,1.3)°; and O-Mn-O = 86.2(4)°.
z_9 (O)C-Mn-N = 92.6(6,2.6) and 177.5(6)°; (O)C-Mn-O = 92.8(5,1.9) and 177.0(5,6)°; O-Mn-N = 87.0(4,8)°; and O-Mn-O = 85.7(3)°.
z_{10} (O)C-Mn-P = 91.4(2,5)°.
z_{11} There are two crystallographically independent molecules.
z_{12} (O)C-Mn-P = 89.8(5,1.7)°.
z_{13} (O)C-Mn-P = 91.5(8,4.3)°.
z_{14} (O)C-Mn-N = 98.9(3,3.9)°; (O)C-Mn-C = 95.5(2,6.8)°; C-Mn-N = 94.7(2,8)°.
z_{15} At 153K; (O)C-Mn-S = 90.6(2) and 103.1(2)°.

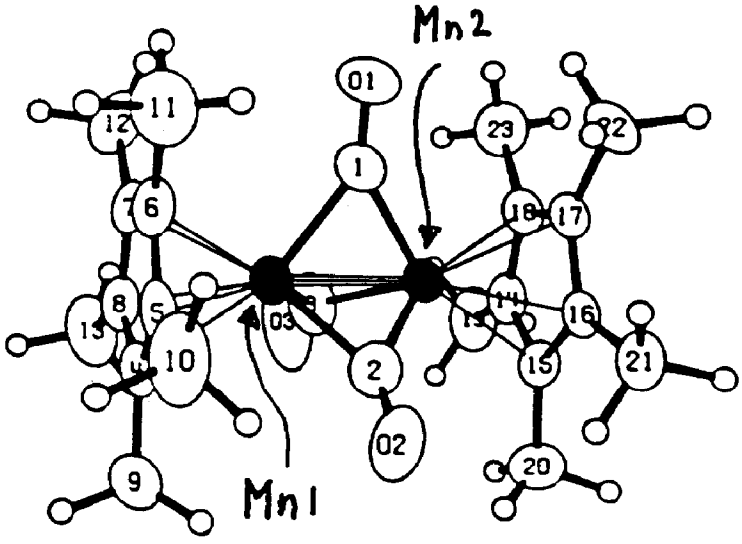

Figure 16. Structure of $Mn_2(\mu\text{-}CO)_3(\eta^5\text{-}C_5Me_5)_2$ Reproduced with permission from Chem. Ber. [254]

atoms within 217.0(1) pm, with Mn-C-Mn angles of 68.5(2)°. This is the shortest Mn-Mn distance found in a manganese complex.

In several cases two ligands serve as the bridges, for example: two $NNSiMe_3$ [255]; two NO [256,257]; NO and CO [258]; two CH_2Ph [262]; CO and C_3H_4 [263]; two CH_2CMe_3 [262]; two CH_2SiMe_3 [262,266]; two Cl [274,277] and $Mn_2(CH_2C_6H_4NMe_2)_4$ [269]. The Mn-Mn distance decreases from 239.2(2) pm [255] to 380.6(3) pm [277], representing a change in bond order from two to zero respectively. Contrary to expectation there is no relationship between Mn-Mn distance and Mn-L-Mn bridge angle, probably due to the variety of bridging ligands involved.

In two cases, $Mn2(\mu_2\text{-tmi})(CO)_8$ [260] and $Mn_2(\mu_2\text{-hdd})(CO)_7$ [261], π-type organic ligands are used for bridging. The Mn-Mn distance in the former (261.5(1)pm) is shorter than that in the latter (265.4(1)pm).

There are examples of manganese centres being bridged by one ligand atom: an organic carbon [206,264,265,267,268,276]; sulphur [272]; arsenic [271,279] and phosphorus [281]. Here there is a tendency for the expected elongation of the Mn-Mn distance with opening of the Mn-L-Mn bridge angle. For example,

273.4(2) pm and 88.0(5)° [206] compared to 380 pm and 131.3(4)° [276], respectively.

Another type of bridge is represented by $Mn_2(CO)_4[\mu\text{-}C(O)CH_2N_2](\mu\text{-dppm})_2.2CH_2Cl_2$ [270], where two non-equivalent manganese atoms, one with MnC_3P_2N chromophore and the other with a MnC_2P_2N chromophore, are held together by a diazomethane ligand using two nitrogen atoms to bridge assymmetrically. An additional two bidentate dppm ligands serve as extra bridges. The manganese atoms in this case are 289.8(2) pm apart.

In orthorhombic $Mn_2(CO)_6(\eta^6\text{-}C_8H_8)$ [273] the eight π-electrons of the cyclooctatetraene ligand are factored into two cis-diene systems over two MnC_3 moieties, with an Mn-Mn distance of 304.5(2) pm.

In another two orthorhombic examples [275,282], the skeletal unit is a pentagonal bipyramidal metallaocarborane cluster of the closo type. In each, two $Mn(CO)_3$ moieties are held together by four carbon atoms and the boron of the borazole ring. In dark purple $Mn_2(CO)_6(\eta^5\text{-}C_4H_4N)$(pcr) [289] a molecule of π-pyrrolyltricarbonylmanganese is N-coordinated with the second manganese atom via the donor electron pair of the pyrrolyl nitrogen atom. The completion of the hexacoordination sphere uses three CO ligands and the formation of a six membered chelate metallocycle, involving an oxy-oxygen and one of the oxygens of the O-nitro group of the picrate anion. A similar structure has been found for $Mn_2(CO)_6(\eta^5\text{-}C_4H_4N)$(acpr) [278].

In another unique case [280], two $Mn(CO)_4$ groups are bridged by an $AsMe_3$ group (Mn-As = 250.8(2) and 248.9(2) pm), and by Mn-As(Me)$_2$-C=C-Mn (Mn-As = 241.0(2) pm and Mn-C = 202.7(7) pm. $F_2C\text{-}CF_2$

Single bridging via two atoms is observed in a number of cases: Mn-N-N-Mn [283]; Mn-S-S-Mn [284]; Mn-P-P-Mn [285]; Mn-As-As-Mn [286] and Mn-C-O-Mn [287,288].

A similar bridge structure involving three atoms is observed where two MnC_7P chromophores are linked by Mn-P-X-P-Mn, where X = O [290] or S [291].

In the remaining examples [292-298] the manganese atoms are joined by multidentate organic ligands, as shown in Figure 17.

The data shows examples of mixed valencies, Mn(II) and Mn(0) [256,257]. Two crystallographically non-equivalent molecules have been found in two cases [289,291]. There are several examples in which two non-equivalent manganese atoms are present [278-280,287,288,296].

Both electronic and steric factors influence the Mn-L bond distance which elongates in the order: 178.5 pm (mean, CO) <202.6 pm ($CONH_2$) <211.9 pm (CH_2CCH_2) <212.7 pm (CH_2Ph_2) <217.7 pm (CH_2SPh); and 165.8 pm (NO) <199.2 pm (NO_2) <228.4 pm (tmeda). In general the Mn-L(bridge) bond distances are longer

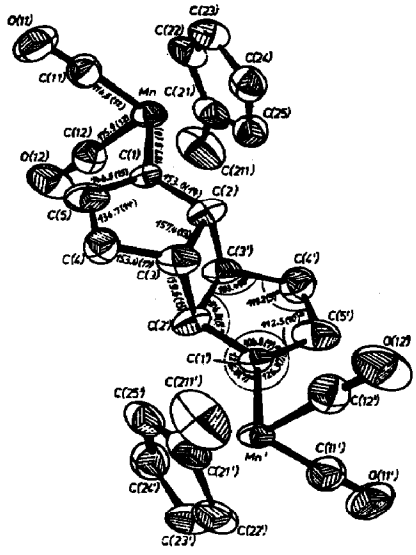

Figure 17. Structure of [{Mn(CO)$_2$(η^5-cp*)}$_2$(μ_2-cbdcp)] Reproduced with permission from Z. Anorg. Allg. Chem. [297]

than the Mn-L(terminal) distances, for example: 206.7 and 178.5 pm (L = CO), 185.4 and 165.8 pm (L = NO), 216.6 and 212.7 pm (L = C-Ligand), respectively.

In the binuclear examples where the manganese atoms are bridged by one or two ligating atoms, there is a tendency for the Mn-Mn distance to elongate as the Mn-L-Mn angle opens. The Mn-L distances also tend to be longer in the binuclear than in the mononuclear derivatives. For instance, the mean value of the Mn-C(CO), Mn-C(C-ligand) and Mn-P distances are 178.5, 212.7 and 249.4 pm respectively for the binuclear compounds (Table 13), compared to 178.0, 187.0 and 222.6 pm for the mononuclear compounds (Table 11). On the other hand the mean Mn-C(cp) distance of 213.7 pm found in the binuclear organometallics is somewhat shorter than that found in the mononuclear ones (215.0 pm).

(C) Tri- and Tetranuclear organometallic compounds

The crystallographic and structural data for these compounds is collected in Table 14, arranged in increasing Mn-Mn distance and degree of aggregation. The crystal structure of [Mn$_3$(μ_3-NH)(μ_2-NO)$_3$(η^5-cp*)$_3$](BF$_4$) [299] is shown in Figure 18. The central Mn$_3$(NO)$_3$ core is an equilateral triangle of metal atoms triply bridged by three nitrosyl ligands along the edges (Mn-N = 186.0(3)pm). The

Table 14 Crystallographic and structural data for tri- and tetranuclear manganese organometallic compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	M-M(pm) M-L-M [°]	M-M-M L-M-L [°]	Ref
$[Mn_3(\mu_3\text{-}NH)(\mu_2\text{-}NO)_3.(\eta^5\text{-}cp^*)_3].(PF_6)$						MnC_5N_3	$(\eta^5)C^b$ d ON^c 186.0(3) HN^c 187.2(3)	250.27(7) d 83.95(12)		299
$Mn_3(\mu_3\text{-}NO)(\mu_2\text{-}NO)_3.(\eta^5\text{-}cp)_3$	m	$P2_1/c$	4	1334.1(4) 795.1(2) 1683.7(7)	107.73(3)	MnC_5N_3	C 215.1(8,25) $(\mu_2)N^c$ 184.8(4,9) $(\mu_3)N^c$ 192.9(4,12)	250.6(1,4) 85.4(2,4) 81.0(2,2)	60.00(3,14) 95.0(2,3.3)	300
$[Mn_3(\mu_3\text{-}NOH)(\mu_2\text{-}NO)_3.(\eta^5cp^*)_3](BF_4)$						MnC_5N_3	$(\eta^5)C$ d $(\mu_2)N^c$ 185.6(4) $(\mu_3)N^c$ 187.3(3)	250.83(9) d 84.1(2)		299
$Mn_3(\mu_4\text{-}MeC_5H_6)_4$	tr	P1	2	693.7(1) 742.7(1) 2394.0(3)	83.54(1) 83.77(1) 64.15(1)	$Mn^{II}C_4$	C^c 233.4(8,13)	251.6(2,1)	177.51(6) 109.56(27,8.79)	301
						$Mn^IC_{10}(2x)$	C_c 210.3(8,58) C^c 215.7(8,9)			
$Mn^{II}_3(\mu_2\text{-}mes)_4(mes)_2$	tr	P1	2	1285.0(3) 2032.7(4) 1140.7(3)	95.11(2) 114.00(2) 98.77(2)	MnC_4	C^c 234(1,1)	285.1(3,0)	178.8(1) 109.9(4,15.1)	302
						$MnC_3(2x)$	C_c 211(1,1) C^c 220(1,2)		119.4(4,13.2)	
$Mn_3(\mu\text{-}\eta^5\text{-}C_4H_4N)_2(CO)_8I$	m	$P2_1/c$	4	1104.0(2) 1496.0(2) 1402.8(2)	106.15(1)	MnC_3N_2I	OC 181(1,3) I 272.2(2) N^c 211.7(8,2)	385.3(2,37)		303
						$MnC_7N(2x)$	OC 180(1,4) C_c 213(1,3) N^c 213.4(8,3)			
$Mn_3(CO)_6(\mu\text{-}\eta^5\text{-}C_4H_4N)_2.(\mu\text{-}n\text{-}BuCO)$	m	$P2_1/n$	4	850.3(1) 1365.7(3) 2118.5(4)	100.84(2)	MnC_3N_2O	OC 177(4,8) O 198(2) N^c 211(3,0)			304
						MnC_7N	OC 168(4,7) $(\eta^5)C$ 217(3,3) N 217(3)			

Table 14, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromo-phore	M-L [pm]	M-M(PM) M-L-M [°]	M-M-M L-M-L [°]	Ref
						MnC_7N	OC 169(4,3) (η^5)C 218(4,7) N 216(3) BuOC 196(3)			304
$Mn_3(CO)_9(\mu\text{-}\eta^5\text{-}C_4H_4N)_2$. .(dpac)	m	$P2_1/c$	4	1553.2(5) 959.4(3) 2160.9(8)	97.28(3)	MnC_3N_2O	OC 179.6(14,46) O$_c$ 202.0(8) N^c 209.9(9,9)	135.3(5,1.9)		305
						$MnC_7N(2x)$	OC 173.6(20,93) (η^1)C$_c$ 211.9(14,27) N^c 210.1(9,6)			
[{$Mn(CO)_2(\eta^5\text{-}cp^*)$}$_4$. .($\mu_3$-As)$_2$]	m	$P2_1/c$	4	946.0(6) 1289.6(6) 2738(6)	113.75(6)	$MnC_7As(2x)$	OC d (η^5)C$_c$ d As^c 224.3(3,1)			306
						$MnC_6As_2(2x)$	OC d (η^5)C$_c$ d As^c 226.6(3,7)	287.5(3) 78.8(1,1)		
[{$Mn(CO)_2(\eta^5\text{-}cp)$}$_4$. .($\mu_2$-As)$_2$]	m	C2/c	4	1919(3) 988(1) 1643(2)	111.31(9)	MnC_7As	OC 181(2,3) (η^5)C$_c$ 216-217(1) As^c 227.1(4,7)	132.8(1)		306

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom (ligand)
d not given.

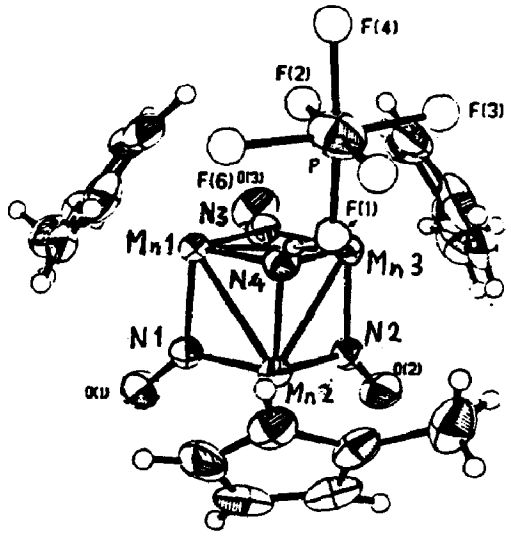

Figure 18. Structure of $[Mn_3(\mu_3\text{-}NH)(\mu_2\text{-}NO)_2(\eta^5\text{-}cp^*)_3](PF_6)$ Reproduced with permission from J. Amer. Chem. Soc. [299]

cyclopentadienyl rings are located off the apices of the metal triangle. The Mn-Mn bond distance of 250.27(7) pm is the shortest of the trinuclear derivatives. Two other similar derivatives have slightly longer Mn-Mn distances, 250.6 pm [300] and 250.83(9) pm [299].

An almost linear array of three manganese atoms is found in two cases with angles of 177.51(6)° [301] and 178.8(1)° [302], and average Mn-Mn distances of 251.6(2,1) and 285.1(3,0) respectively.

In a bright orange-red trinuclear iodide complex [303] two $Mn(CO)_3(\eta^5\text{-}C_4H_4N)$ moieties act as N-ligands at the third (and central) Mn atom (Mn-N = 211.7(8,2) pm, which also coordinates the iodide (Mn-I = 272.2(2)pm) and three CO groups (Mn-C = 181(1,3) pm. The Mn-Mn distance of 385.3(2,37)pm rules out a metal-metal bond in this case. There are two other examples with the same outer chromophores [304,305].

There are two examples of tetranuclear complexes bridged by arsenic. In black $[Mn(CO)_2(\eta^5\text{-}cp^*)]_4(\mu_3\text{-}As)_2$ [306] each arsenic bridges three metal atoms in a trigonal planar array. For monoclinic $[Mn(CO)_2(\eta^5\text{-}cp)]_4(\mu_2\text{-}As)_2$ [307], the structure of which is shown in Figure 19, a diarsenic bridge links two pairs of metal atoms.

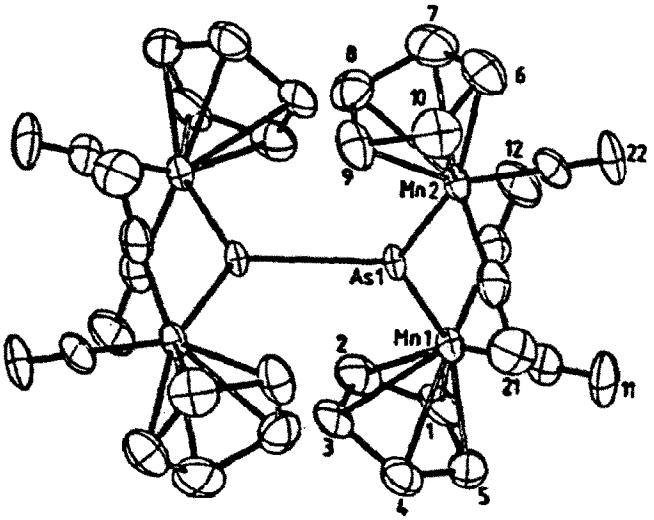

Figure 19. Structure of $\{Mn(CO)_2(\eta^5\text{-cp})\}_4(\mu_3\text{-As})_2$
Reproduced with permission from Organometallics [307]

The mean value of the Mn-C(cp) distances is longer for the trinuclear compounds than was observed for the binuclear ones (213.7 pm and 215.1 pm respectively). By contrast, the mean Mn-C(CO) distance in the former (175.8 pm) is shorter than in the latter (178.5).

(D) Hetero-binuclear organometallic compounds

The data for these compounds is shown in Table 15, and can be subdivided by bridge type. In several cases a manganese atom is directly bonded to another metal atom without a ligand bridge, for example Mn-Ge [312] with a bond distance of 252.4(4) pm, and three examples of Mn-Sn [313-315]. Another three examples involve direct Mn-Mo bonds [320-322], and other transition metal examples include Mn-Re (297.2(1) pm) [327], Mn-Fe(284.0(4) pm and 284.5(4)pm [334] and Mn-Pt (265.9(2)pm) [347].

In several cases, a single bridge is found, for example: H atom [310,311,-319]; a carbon donor [318,323,326,329,331,333); iodine between Mn and Pb moieties [343]. As the bridge angle Mn-L-M opens, the Mn-M distance increases, as expected: 58.2(1)° and 260.3(1)pm Mn-I-Pt [343]; 79(1)° and 281.7(3)pm Mn-C(CO)(Ph)-Re [329]; 141(5)° and 333.0(2)pm Mn-H-Nb [319].

Table 15 Crystallographic and structural data for heterobinuclear manganese organometallic compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromo-phore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
$Mn\{C(OAlBrBr_2)CH_3\}(CO)_4$	m	$P2_1/c$	4	683.5(2) 1637.4(6) 1227.8(4)	 94.18(7) 	MnC_5Br	OC[b] 185(2,6) C[c] 195(2) Br 258.0(4)	90.7(9,1.6) 177.0(1) d	308
$Me_2Ga(dmpz)(tpe)Mn^I(CO)_3$	tr	P1	2	949.11(5) 1043.23(6) 1176.18(7)	86.17(1) 69.547(5) 81.402(4)	MnC_3NOS	OC 179.9(4,10) N 207.7(3) S 238.9(1) O[c] 204.7(2)	88.6(2,5) e	309
$(\eta^5\text{-cp}^*)(CO)_2Mn(H)SiFPh_2$[f]	m	$P2_1/c$	4	1622.6(8) 703.2(3) 2020.3(14)	 128.55(3) 	MnC_7HSi	OC 178.9(3) (η^5)C d H 156.9(4) Si 235.2(4)	89.7(1) f	310
$(\eta^5\text{-cp}^*)(CO)_2Mn(H)SiCl_3$	m	$P2_1/C$	4	1206.6(5) 845.3(3) 1638.6(6)	 131.85(3) 	MnC_7HSi	OC 179.4(7,4) (η^5)C 211.5-214.0(6) H 147(3) Si 225.4(1)	87.6(3) g	311
$Mn(CO)_5GePh_3$		A2/a	8	1123(2) 1148(4) 3310(20)	 94(1) 				108
$MePh(1\text{-np})Ge(CO)_4Mn\{C(Me)(OEt)\}$	or	$P2_12_12_1$	4	929.4(3) 3205.1(10) 809.9(2)	 	MnC_5Ge	OC 175.9(26,42) C 195.1(20) Ge 252.4(4)	89.6(10,8) 166.6(10) h	312
$Ph_3SnMn(CO)_5$	m	C2/c		1591(1) 1632(1) 3312(2)	 95.0(1) 				313
$Me_3SnMn(CO)_5$	m	$P2_1/n$	4	701.8(9) 1338.9(17) 1466.2(20)	 114.30(3) 	MnC_5Sn	OC 180.6(12,48) Sn 267.4(2)	94.2(6,13.4) 168.7(6,1.6)	314

Table 15, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
$BrMe_2SnMn(CO)_3(PPh_3)_2$	m	$P2_1/m$	4	2375.1(5) 1627.9(2) 1030.6(3)	 98.03(2) 	MnC_3P_2Sn	OC 172.4(32,146) P 231.8(9,47) Sn 265.9(6)	not given 156.8(18) j	315
$\{(CO)_3Mn[\eta^5\text{-}C_6H_3(CH_2NMe_2).(CHNCHMeC(O)N\text{-}CHMeCOO)Cu]\}$ [k]	m	$P2_1$	4	971.2(2) 2228.6(4) 950.17(7)	 94.44(2) 	MnC_6	OC 178(2,4) (η^5)C 215(2,6)	90(1,1)	316
						MnC_6	OC 180(2,1 (η^5)C 214(2,5)	90(1,3)	
$(\eta^5\text{-cp})(CO)_2\{\eta^5\text{-cp})[\eta^5\text{-}C_5H_4PPh_2].TiCl_2\}Mn$	or	Pnma	4	2043.6(9) 1233.6(6) 1041.2(6)		MnC_7P	OC 174(1,0) (η^5)C 215.0(8,10) P 226.6(4)	91.0(6) l	317
$(\eta^5\text{-cp})_2Nb(CO)(\mu\text{-CO})Mn(CO)_4$	m	$P2_1/c$	4	829.2(3) 1623.2(5) 1161.5(4)	 92.40(2) 	MnC_5Nb	OC 182.7(5,35) Nb 317.6(1)	92.9(2,11.3) 164.5(2,9.2) m	318
$(\eta^5\text{-cp})(CO)_2Mn(\mu\text{-H})Nb(CO).(\eta^5\text{-cp})$ [n]	m	$P2_1/n$	4	908.8(2) 1423.9(4) 1280.1(3)	 95.03(2) 	MnC_7N	OC 173.1(9,2) (η^5)C 213.3(12,37) H[c] 156(8)	n	319
$(\eta^5\text{:}\eta^1\text{-cp})(\eta^5\text{-cp})(CO)MoMn(CO)_4$	tr	P1	2	805.6(1) 932.2(3) 1192.7(2)	98.44(3) 82.97(3) 123.39(2)	MnC_5MO	OC 182.1(4,35) (η^1)C 200.5(4) Mo 296.05(8)	91.7(2,5.9) 177.2(2) o	320
$(\eta^5\text{-}C_5H_4PPh_2)(CO)_3MoMn(CO)_4$	or	Pbca	8	1178.2(2) 1721.5(3) 2312.9(6)	 	MnC_4PMo	OC 182.9(5,37) P 227.8(1) Mo 305.4(i)	85.8(2,12.4) p	321
$(\eta^5\text{-cp})(CO)_3MoMn(CO)_5$	m	$P2_1/c$	4	1462(2) 888(1) 1162(2)	 94(1) 	MnC_5Mo	OC 174(2,4) Mo 308(1)		322
$[(\eta^5\text{-cp})MoMn(\mu\text{-H})(\mu\text{-}PPh_2)(CO)_6]$	m	P2/a	4	1592.2(2) 854.4(1) 1833.0(2)	 113.79(1) 	MnC_4PHMo	OC not given P 229.4(2) H[c] not given Mo 308.8(1)		323

Table 15, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
[(η^5-cp)MoMn{μ-6:η^3-$CH_2C(Me)$. .CHMe}(μ-PPh_2)(CO)$_4$]	m	$P2_1/c$	4	1033.7(1) 1574.3(1) 1528.2(1)	 102.49(1) 	MnC_4PMo	OC 180.1(4,37) C 234.6(4) P 226.7(1) Mo 280.0(1)		323
[(η^5-cp)MoMn{μ-6:η^4-CHCHCH$_2$. .PPh_2(CO)$_4$]	m	$P2_1/n$	4	1170.9(1) 1585.7(1) 1267.0(1)	 100.45(1) 	MnC_6Mo	OC 178.8(3,11) LC 217.2(3,91) Mo 268.0(1)		323
[(η^5-cp)MoMn{μ-C(O)C_6H_{11}}. .(μ-PPh_2)(CO)$_5$]	m	$P2_1/c$	4	911.8(3) 1463.2(4) 2068.7(3)	 101.25(4) 	MnC_3DPMo	OC 178.4(12,40) O 202.7(6) P 226.5(3) Mo 296.3(2)		324
[(η^5-cp)MoMn{μ-C(O)$CH_2CH_2CH_3$}. .(μ-PPh_2)(CO)$_6$]	m	$P2_1/n$	4	2866.9(6) 980.7(2) 958.8(2)	 93.23(3) 	MnC_5P	OC 178(3,3) C 204.3(19) P 238.8(6)		324
(η^5-cp)(CO)$_3$WMn(CO))$_3$	m	$P2_1/n$	4	970(5) 2485(4) 704(2)	 115.2(1) 				108
(CO)$_3$Mn(μ-$C_5H_4COCH_2$)W(CO)$_3$. .(η^5-cp)	tr	P1	2	686.6(2) 2086.0(6) 690.7(2)	97.20(3) 67.77(7) 97.35(3)	MnC_8	OC 180.3(22,45) (η^5)C 212.3(23,50)		325
(η^5-cp)(CO)$_2$MnW(μ-C=CHCOOMe). .(CO)$_4$	m	$P2_1/c$	4	752.3(3) 1945.6(6) 1117.5(4)	 96.04(3) 	MnC_8W	OC 178.9(6,16) (η^5)C 214.3(6,28) C 190.3(5) W 299.39(8)	88.5(3) q	326
cis-(CO)$_5$MnRe(CO)$_4${C(OMe)Me}	tr	P1	2	899.9(5) 1309.3(2) 820.2(2)	111.24(2) 112.22(3) 84.41(3)	MnC_5Re	OC 183.4(8,38) Re 297.2(1)	92.6(4,5.7) 168.6(3,3.1) r	327
(CO)$_3$Mn(η^5-C_4H_4N)Re(η^5-cp). .(CO)$_2$	m	$P2_1/b$	4	634.9(2) 1365.3(5) 1712.8(3)	 97.55(2)	MnC_7N	OC 185(3,2) C 218(2,2) N 216(2)	91(1,3) not given	328

Table 15, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
(η^5-cp)(CO)$_2$Mn{μ-C(CO)Ph}. .Re(CO)$_4$	m	$P2_1/c$	4	1115(1) 1464(1) 1657(2)	136.79(8)	MnC_7Re	OC 184(4,3) (η^5)C^c 216(2,5) C^c 221(3) Re 281.7(3)	86(1) s	329
$MnRe(CO)_8\{(CO)C_6H_3PPh_2\}$	m	$P2_1/c$	4	1235.7(6) 1125.8(6) 2144.3(5)	111.40(3)	MnC_5O	OC 185(1,4) C 205(1) O 207(1)	92.3(6,4.7) 168.7(6) t	288
[η^5-cp)(CO)FeMn(CO)$_4$](μ-CH$_2$). .(μ-CO)	m	$P2_1/m$	2	828.2(1) 1000.2(2) 860.4(1)	115.70	MnC_6Fe	OC 184.6(5,23) H$_2$C^c 208.7(3) OC^c 208.7(3) Fe 261.78(10)	92.5(1,5.1) 179.6(2) u_1	340
(η^5-cp)(CO)FeMn(CO)$_4$](μ-CH$_2$). .(μ-CO)	m	Cc	4	1540.2(2) 617.31(7) 1410.4(2)	107.36	MnC_6Fe	OC 183.3(6,39) H$_2$C^c 208.5(5) OC^c 213.4(5) Fe 261.27(9)	92.2(3,8.0) 178.3(3) u_2	330
(η^5-cp)(CO)$_2$Mn(μ^2-C=CHCOOMe). .Fe(CO)$_4$	m	$P2_1/c$	4	1303.5(2) 811.6(1) 1543.2(2)	97.17(1)	MnC_6Fe	OC 178(2,3) (η^5)C^c 215(2,3) C^c 195(1) Fe 270.3(4)	90.8(9) v	331
[(μ-H)FeMn(CO)$_8$.(C$_5$H$_4$N-2-CH=N-t-Bu)]	or	$P2_12_12_1$	4	864.3(6) 1414.3(5) 1512.0(5)		MnC_3N_2HFe	OC 181.4(1,1) N^c 205.6(1,5) H^c 173(2) Fe 274.65(3)	89.55(7,2.68) x	332
(η^5-cp)(CO)$_2$Mn{C(CO)CHPh}. .Fe(CO)$_3$	m	$P2_1/c$	4	1034.4(1) 798.55(3) 2179.6(2)	102.924(9)	MnC_9Fe	OC 177(2,3) (η^5)C^c 218(2,1) C^c 203(2) Fe 276.0(4)	88.4(8) y	333
(η^5-cp)(CO)$_2$FeMn(CO)$_5$[k]	m	$P2_1/b$	8	722.0(6) 3038.7(8) 1249.8(2)	90.21(10)	MnC_5Fe	OC 181.0(25,62) Fe 284.0(4)	92.0(1.0,4.2) 172.4(1.0,1.2) z	334

Table 15, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
						MnC_5Fe	OC 181.0(25,60) Fe 284.5(4)	91.9(1.0,4.6) 173.3(1.0,3) z_2	334
$(\eta^5\text{-cp})(CO)_2Mn(\mu_2\text{-}CS_2)Fe.(CO)_2(PMe_2Ph)_2$	m	$P2_1/c$	4	1041.1(1) 976.2(2) 2819.4(5)	93.090(10)	MnC_7S	OC 176.5(7,15) (η^5)C 214.4(8,33) S 226.0(2)	not given	335
$(\eta^5\text{-cp})Fe(\eta^5\text{-}C_5H_4)CH_2(Me)NCH_2.Mn(CO)_4$	or	$P2_12_12_1$	4	1015.2(2) 2134.8(4) 810.4(1)		MnC_5N	OC 184(2,5) C 205(1) N 205(1)	90.6(6,12.3) 171.9(5) z_3	336
$(CO)_3Mn(\eta^5\text{-}C_5H_4\text{-}n')Fe(\eta^5\text{-cp}).(CO)_2$	m	$P2_1/c$	4	859.2(2) 1352.1(2) 1248.1(3)	94.92(2)	MnC_8	OC 179.0(8,3) (η^5)C 215.5(7,61)	92.1(4,8)	337
$(CO)_3Mn(\eta^5\text{-}C_5H_4\text{-}n')Fe(\eta^5\text{-cp}).(CO)(PPh_3)$	m	$P2_1/C$	4	1078.3(2) 1429.4(4) 1810.5(4)	92.77(2)	MnC_8	OC 174(2,4) (η^5)C 217(2,8)	93.1(9,2.5)	337
$(\eta^5\text{-cp})Co(\mu_2\text{-NO})_2Mn(\eta^5\text{-cp})^k.(PMe_3)$	tr	P1	4	974.11(7) 1300.04(8) 1367.68(14)	77.554(7) 77.960(7) 68.942(6)	MnC_5N_2PCo	P 226.7(1) $(\eta^5)C_c$ not given N^c 180.2(1,5) CO 244.7(1)	z_4	338
						MnC_5N_2PCo	P 227.0(1) $(\eta^5)C_c$ not given N^c 181.0(2,2) Co 244.4(1)	z_5	
$(CO)_3Co(\mu_2\text{-}Ph_2C_4Me_2)Mn(CO)_3$	m	$P2_1/c$	4	1630.8(3) 887.5(2) 1557.4(4)	93.44(2)	MnC_7Co	OC 179.4(4,9) C 217.8(3,8) C^c 209.9(3,1) Co 254.88(8)	not given	339
$(\eta^5\text{-cp})(CO)Mn(\mu_2\text{-}CO)_2Rh(CO).(\eta^5\text{-}C_5Me_5)$	or	Pnam	4	1685.1(12) 933.8(5) 1156.6(9)		MnC_6Rh	OC 178.4(12) (η^5)C 215.1(9,11) OC^c 186.6(7,0) Rh 270.3(2)	93.1(3) z_6	340

Table 15, cont. (6)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromophore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
(η^5-cp)(PPr_3)Rh(μ-C=CH_2).(μ-CO)Mn(CO)(η^5-cp)	m	$P2_1/c$	4	1604.4(6) 843.3(3) 1677.0(7)	101.94(3)	MnC_6Rh	OC not given (η^5)C$_c$ not given OC^c 190.1(3) Rh 266.7(1)	z_7	341
[(η^5-cp)Ir{μ-C(Ph)O}{μ-C(Me)O}.{μ-PPh_2}$Mn(CO)_3$].0.5C_6H_6	m	$P2_1/c$	4	2108.9(4) 857.6(2) 1653.0(2)	102.50(1)	MnC_3O_2P	OC 180.4(11,33) C(Me)O 202.8(6) C(Ph)O 204.0(6) Ph_2P 234.8(3)	90.0(5,1.9) z_8	342
(PBu_2Me)($CH_2CH_2CH_2CO$)Pt(μ-I).$Mn(CO)_4$	or	Pbca	8	1463.4(5) 1954.6(18) 1632.5(5)		MnC_4IPt	OC$_c$ 182(1,4) I 268.9(2) Pt 260.3(1)	94.6(4,6.7) 159.9(4) z_9	343
[(PMe_3)(4-MeC_6H_4S)Pt(μ-CO).{μ-C(PMe_3)C_6H_4Me-4}Mn(CO)(η^5-cp)	or	$Pca2_1$	4	1948.2(4) 1282.7(4) 1164.9(2)		MnC_6Pt	OC 176(1) (η^5)C$_c$ 215(1,3) OC^c 185.9(9) C^c 204.7(9) Pt 262.6(1)	86.1(4) z_{10}	344
[(PMe_3)$_2$Pt{μ-C(PMe_3)C_6H_4Me-4}.$Mn(CO)_2$(η^5-cp)](BF_4)	tr	P1	2	1087.7(2) 1023.0(2) 1391.7(4)	92.80(2) 95.28(2) 90.08(2)	MnC_6Pt	OC 176.4(7,11) (η^5)C$_c$ 215.7(7,22) C^c 210.7(5) Pt 264.5(1)	98.3(4) z_{11}	344
[(PMe_3)$_2$Pt(μ-CC_6H_4Me-4)$Mn(CO)_2$.(η^5-cp)](BF_4).CH_2Cl_2	m	$P2_1/c$	4	1043.4(4) 1933.4(7) 1490.1(7)	94.42(4)	MnC_6Pt	OC 181(1,1) (η^5)C$_c$ 215(1,2) C^c 182.9(8) Pt 262.8(1)	88.2(5) z_{12}	345
($PMePh_2$)$_2$Pt(μ-CS)$Mn(CO)_2$(η^5-cp)	m	$P2_1/c$	4	1665.5(4) 968.4(3) 2140.9(5)	114.57(2)	MnC_6Pt	OC 178.4(10,14) (η^5)C$_c$ 216.1(9,10) SC^c 187.8(8) Pt 264.1(1)	91.8(4) z_{13}	346
[(PMe_3)$_2$Pt{μ-(1-σ,1-2-$\eta^{z_{14}}$-C=$CHCH_2CH_2C$)}$Mn(CO)_4$]	m	$P2_1/n$	4	935.7(5) 1284.4(10) 1598.9(9)	98.14(4)	MnC_6Pt	OC$_c$ 182.8(6,40) C^c 222.4(5,27) Pt 269.09(7)	92.5(2,6.7) 172.3(2) z_{14}	347

Table 15, cont. (7)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] γ[°]	Chromo-phore	Mn-L [pm]	(O)C-Mn-C(O) cis-[°] trans-[°]	Ref
[(PMe$_3$)$_2$Pt{μ-σ,1-2-$\eta^{z_{15}}$-C=CH$_2$CH$_2$C)}Mn(CO)$_4$]	tr	P1	2	942.9(5) 1211.3(4) 972.9(6)	93.97(14) 115.45(4) 98.83(3)	MnC_4Pt	OC 181.5(10,35) C^c 228.4(16,9) Pt 265.9(2)	93.7(6,7.1) 161.3(5) z_{15}	347
(η^5-cp)$_3$U(μ-OC=CHPMe$_2$Ph)Mn.^{k} .(CO)$_2$(η^5-cp)	or	Pba2	8	2242.3(5) 3532.8(7) 864.8(3)		MnC_5 MnC_5	OC not given (η^5)C$_c$ not given C^c 202(4) OC not given (η^5)C$_c$ not given C^c 198(3)		348

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom (ligand).
d (O)C-Mn-C = 89.2(9,1.7) and 178.3(8)°; (O)C-Mn-Br = 89.4(6,3.0) and 117.2(6)°; C-Mn-Br = 90.8(5)°.
e (O)C-Mn-N = 94.1(1,1.8) and 175.2(1)°; (O)C-Mn-O = 92.0(1,1.8) and 177.2(1)°; (O)C-Mn-S = 94.3(1,6) and 176.1(1)°; N-Mn-S = 84.51(8)°; O-Mn-S = 83.74(6)°.
f By neutron diffraction, at 120K; (O)C-Mn-H = 76.4(2) and 108.3(2)°; (O)C-Mn-Si = 78.1(1) and 115.2(1)°; (O)C-Mn-cp = 123.7(-,3)°; H-Mn-H = 50.0(2)°; H-Mn-Cp = 121.9°; Si-Mn-Cp = 115.6°.
g (O)C-Mn-Si = 81.1(2) and 113.3(2)°; (O)C-Mn-H = 75(2) and 114(2)°.
h (O)C-Mn-C = 90.8(11) and 178.1(11)°; (O)C-Mn-Ge = 84.4(8,2.6) and 178.0(8)°; C-Mn-Ge = 91.7(8)°.
i (O)C-Mn-Sn = 84.4(4,2.0) and 178.0(4)°.
j (O)C-Mn-Sn = 78.5(7,3.7) and 167.2(8)°; P-Mn-P = 168.7(4)°; P-Mn-Sn = 95.6(3,2.3)°.
k There are two crystallographically independent molecules.
l (O)C-Mn-P = 80.2(4) and 106.8(3)°; (O)C-Mn-Cp = 123.6°; P-Mn-Cp = 120.7°.
m (O)C-Mn-Nb = 60.6(2), 92.7(2,2.0) and 161.1(2)°.
n At 238K, (O)C-Mn-H = 102(3,1)°.
o (O)C-Mn-C = 90.2(2), 107.9(2) and 154.5(2)°, (O)C-Mn-Mo = 94.6(2,11.1) and 156.2(1)°.
p (O)C-Mn-P = 91.9(2,5.4) and 165.7(2)°; (O)C-Mn-Mo = 89.0(2,2.2) and 174.1(2)°.
r (O)C-Mn-Re = 84.3 (2,2.9) and 177.3(3)°.
q (O)C-Mn-C = 80.0(2) and 113.1(2)°; (O)C-Mn-W = 78.9(2) and 107.8(2)°; C-Mn-W = 45.1(2)°; W-Mn-Cp = 125.0°; (O)C-Mn-cp = 121.6(-,5)°; C-Mn-Cp = 120.5°.
r (O)C-Mn-C^c = 98(1) and 112(1)°; (O)C-Mn-Re = 62(1) and 102(1); C^c-Mn-Re = 51(1)°.
t (O)C-Mn-C = 88.6(5,7.4) and 169.4(5)°; (O)C-Mn-O = 91.1(4,2.6) and 174.6(4)°; C-Mn-O = 79.3(3)°.
u, At 163K; (O)C-Mn-C^c = 89.4(1,4.6) and 177.2(2)°; (O)C-Mn-Fe = 90.2(1,3.5) and 131.02(10)°; C^c-Mn-Fe = 46.70(9)°; C^c-Mn-C^c = 92.70(13)°.

Table 15, footnotes continued

u_2 At 163K; (O)C-Mn-C^C = 88.4(2,6.3) and 174.8(2,3)°; (O)C-Mn-Fe = 89.7(2,3.5) and 129.8(2,1.5)°; C^C-Mn-Fe = 46.40(14,15)°; C^C-Mn-C^C = 91.8(2)°.

v (O)C-Mn-C^C = 84.1(9) and 114.6(8)°; (O)C-Mn-Fe = 72.2(7) and 101.3(7)°; C^C-Mn-Fe = 45.8(5)°.

x (O)C-Mn-N^C = 96.87(7,7.24) and 169.82(7,6.91)°; (O)C-Mn-H^C = 85.2(7,10.1) and 173.6(6)°; (O)C-Mn-Fe = 92.57(5), 117.74(5) and 150.41(5)°; N-Mn-N = 81.81(6)°; N-Mn-H = 80.3(7,1.5)°; N-Mn-Fe = 46.40(4) and 85.76(4)°; H-Mn-Fe = 33.3(7)°.

y (O)C-Mn-C^C = 85.5(8) and 111.0(8)°; (O)C-Mn-Fe = 71.1(6) and 107.1(6)°; C^C-Mn-Fe = 46.4(4)°.

z_1 (O)C-Mn-Fe = 86.5(7,10.3) and 168.6(8)°.

z_2 (O)C-Mn-Fe = 87.0(7,8.6) and 169.2(8)°.

z_3 (O)C-Mn-C = 97.3(5,7.6) and 152.1(4)°; (O)C-Mn-N = 100.0(4,11.7) and 145.4(4)°; C-Mn-N = 40.5(3)°.

z_4 P-Mn-Co = 102.60(2)°; P-Mn-Cp = 122.57(2)°; CO-Mn-Cp = 134.83(4)°.

z_5 P-Mn-Co = 104.42(2)°; P-Mn-Cp = 121.89(2): CO-Mn-Cp = 133.67(1)°.

z_6 (O)C-Mn-Rh = 99.8(4)°; (O)C^C-Mn-Rh = 53.0(2), Rh-Mn-Cp = 139.3°.

z_7 (O)C-Mn-Rh = 55.6(1)°; (CH_2)C-Mn-Rh = 50.1(1)°.

z_8 (O)C-Mn-O = 92.3(4,2.2) and 176.9(4,1.1)°; (O)C-Mn-P = 95.3(3,1.1) and 171.1(3)°; O-Mn-P = 82.3(2,7)°; O-Mn-Ir = 55.3(2,0)°; O-Mn-O = 84.9(2)°; P-Mn-Ir = 40.02(6)°.

z_9 (O)C-Mn-I = 93.0(3,9.0) and 161.9(3)°; (O)C-Mn-Pt = 87.6(3,13.9) and 162.3(3)°; I-Mn-Pt = 60.4(1)°.

z_{10} (O)C-Mn-C = 100.6(5,2.9)°; (O)C-Mn-C(cp) = 84.2(4)-152.4(4)°; (O)C-Mn-Pt = 52.8(3) and 104.5(3)°; C-Mn-C(cp) = 97.1(5,3.6) and 128.1(5,7.9)°; Pt-Mn-C(cp) = 103.1(3)-164.1(5)°; C-Mn-Pt = 52.5(2)°.

z_{11} (O)C-Mn-C = 100.7(3,1.9)°; (O)C-Mn-C(cp) = 86.8(3)-151.4(3)°; (O)-C-Mn-Pt = 59.9(2) and 78.0(2)°; C-Mn-C(cp) = 99.2(2,12.6) and 144.0(3,4.0)°; Pt-Mn-C(cp) = 136.1(2,6.6) and 156.9(2,3.1)°; C-Mn-Pt = 50.3(1)°; (cp)C-Mn-C(cp) = 38.3(3,1.0) and 64.1(3,8)°.

z_{12} (O)C-Mn-C = 91.2(4) and 105.3(4)°; (O)C-Mn-Pt = 59.2(3) and 102.9(4)°; C-Mn-Pt = 48.4(3)°.

z_{13} (O)C-Mn-C(S) = 97.9(4,7.6)°; (O)C-Mn-Pt = 56.2(3) and 97.1(3)°; (O)C-Mn-C(cp) = 87.4(4)-151.2(4)°; Pt-Mn-C(S) = 49.5(2)°; (S)C-Mn-C(cp) = 90.2(3)-154.3(3)°; Pt-Mn-C(cp) = 108..1(3)-168.9(2)°; (cp)C-Mn-C(cp) = 38.4(1,2) and 64.2(2,1)°.

z_{14} At 200K. (O)C-Mn-C = 168.3(2)°; (O)C-Mn-Pt = 64.9(2) and 101.4(2,7.4)°; C-Mn-Pt = 75.2(1)°.

z_{15} At 200K. (O)C-Mn-C = 170.5(5)°; (O)C-Mn-Pt = 72.2(4) and 96.8(4,6.0)°; C-Mn-Pt = 76.1(3)°.

Two ligand atoms are used to bridge in a third set of compounds, giving the following examples; two carbon donors [330,339-341,344-346]; a hydrogen and a nitrogen [332]; two nitrogens of NO ligands [338]. The mean bridge angle ranges from 78° to 110°, while the Mn-M distance ranges from 244.4 to 270.3 pm.

Figure 20 illustrates another type of bridging [324] in which the acyl ligand spans the Mn-Mo vector, bonding through carbon to Mo and oxygen to Mn. In addition there is another bridge via the phosphorus atom of PPh_2. The Mn-Mo distance of 296.3(2) pm is typical for a single bond. The same type of bridge has been found in a similar derivative [324] with a 399 pm Mn-Mo distance. Similar bridges are found in other examples: Mn and Al bridged by $C(O)CH_3$, C to Mn and O to Al, plus a bromine bridge; Mn-N-N-Ga via dmpz, and Mn-O-Ga via tpe [309]. Each of the remaining structures in Table 15 represents a unique structure from a bridge point of view. In a red Fe/Mn derivative [335] a $FeCS_2Mn$ moiety is almost planar, with CS_2 bridge η^2-coordinated to Fe through the C=S bond and σ-bonded to the Mn through the second sulphur atom, as can be seen in Figure 21. A tricyclic arrangement is found in a Mn/Ir complex [342], with three bridges between the two metal atoms and no direct M-M bond (354.3(2)pm).

An overall review of the data confirms a tendency for the Mn-M distance to increase as the bridge angles increase. Also, the mean Mn-L(terminal) distance is shorter than the Mn-L(bridge) distance, which is affected by both steric and electronic factors. Thus the mean Mn-L(bridge) distances elongate in the order:

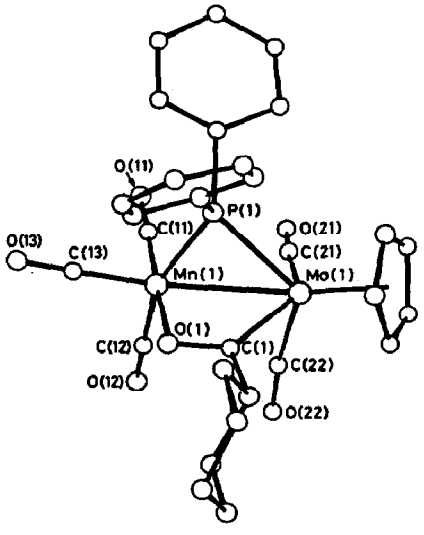

Figure 20. Molecular Structure of $(\eta^5\text{-cp})MoMn\{\mu\text{-}C(O)C_6H_{11}\}(\mu\text{-}PPh_2)(CO)_5$
Reproduced with permission from J. Chem. Soc., Chem. Commun. [324]

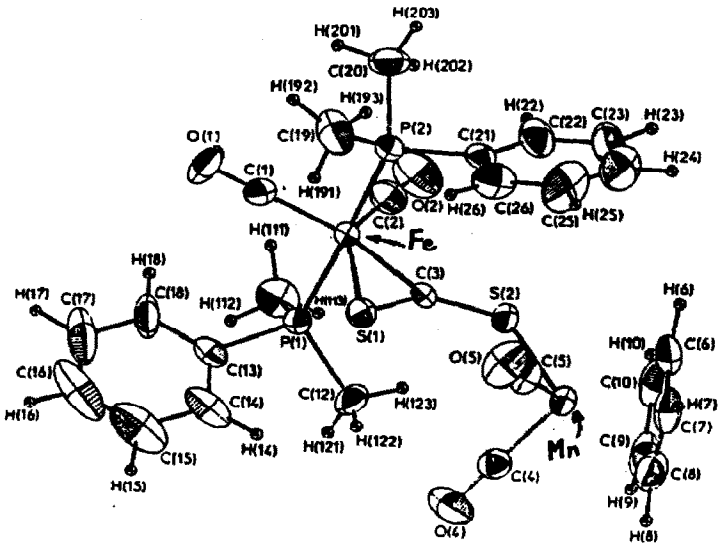

Figure 21. Structure of $(\eta^5\text{-cp})(CO)_2Mn(\mu_3\text{-}CS_2)Fe(CO)_2(PMe_2Ph)_2$ Reproduced with permission from Inorg. Chem. [335]

173pm(H) <186.9pm(NL) <195.6pm(CO) <203.7pm(OL) <205.4pm(Cl)<258.0pm(Br) <268.98pm(I).

The Mn-M average distances are observed to increase in the order: 248.0pm(Mn-CO) <252.4pm(Mn-Ge) <264.2pm(Pt) <266.6pm(Sn) <271.4pm(Fe) <278.1pm(Rh) <289.5pm(Re) <294.6pm(Mo) <299.4pm(W) <325.3pm(Nb).

A red monoclinic isomer and a yellow triclinic isomer are found for a Mn/Pt complex [347]. Two crystallographically independent molecules are found in four examples [316,334,338,348]. In both cases the major difference is one of degree of distortion, thus representing distortion isomerism.

The mean Mn-C(CO) distance is 179.6pm (range 157.8 to 187.0pm), and the mean Mn-C(cp) distance is 214.2pm (207.3-221.6pm). Both are somewhat longer than that observed for the homobinuclear derivatives. By contrast, the mean Mn-C(CO, bridge) distance is longer in the latter than in the former.

(E) Hetero-oligonuclear organometallic compounds

The data for these compounds is listed in Table 16 in order of increasing number of metal atoms. There are several polymetallic derivatives in this series [306,311,350-358] but few have a direct Mn-Mn or Mn-M bond.

A black, sulphur bridged MnCr complex consists of a mononuclear Mn(cp)$(CO)_2$ unit and a binuclear $[Cr(cp)SCMe_3]_2S$ unit, triply bridged by three sulphur atoms such that the manganese is a "piano-stool" configuration. The structure is illustrated in Figure 22.

Some of the hetero-trinuclear derivatives contain two manganese atoms and one other metal [326,359-365). A few molecules have a bent Mn-M-Mn, M = Si [359], M = Ti [362]. In four examples the bent Mn-M-Mn framework is bridged by another group, for example: carbonyl between outer Mn atoms [361]; the C of CH_2Se, where Se is the M atom [364]; hydrogen between a central Mn and outer Ta [363]; carbon donors between each pair of metal atoms [326]. In another example [365], two manganese and one molybdenum are linked by an arsenic atom in a trigonal planar array. In only three examples is there evidence of a Mn-Mn bond, these being at 285.4(2)pm [361], 293.8(1)pm [363] and 307.0(1)pm [365]. The mean Mn-M distances are: 237.1(2,111)pm (M = Ge [360,361]; 243.0(2,59)pm(Se) [364]; 301.7(1,53)pm(Mo) [326,365].

The mean Mn-C(CO) distance of 178.6 pm in the hetero-trinuclears is longer than that of the homo-trinuclear compounds (Table 14). However, the mean Mn-C(cp) distance of 214.9 pm is about 0.2 pm shorter.

There are five examples of hetero-tetranuclear compounds with Mn_2M_2 units: Mn_2Hg_2 [366]; Mn_2Cr_2 [367]; Mn_2Re_2 [368,369]; Mn_2Yb_2 [370]. Only in $\{(\eta^5\text{-cp})Cr(SCMe_3)\}_2SMn_2(CO)_8$ [367] is a Mn-Mn distance smaller than 300 pm

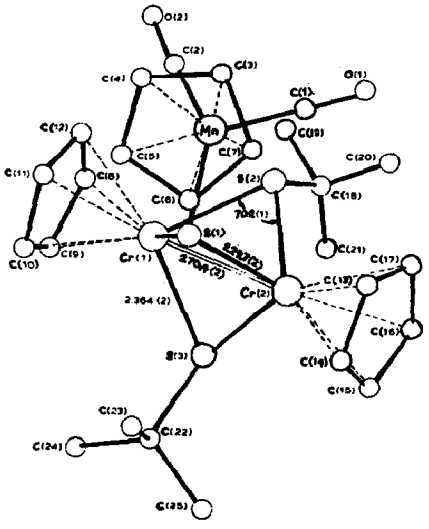

Figure 22. Structure of $\{(\eta^5\text{-cp})Cr(SCMe_3)\}_2(\mu_3\text{-S})Mn(CO)_2(\eta^5\text{-cp})$
Reproduced with permission from J. Organomet. Chem. [351]

Table 16 Crystallographic and structural data for hetero-oligonuclear organometallic compounds[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	(O)C-Mn-C(O) [°]	Ref
$[(CO)_3Mn(CHOAlMe_2N\text{-}t\text{-}BuPPh_2).(PPh_2N\text{-}t\text{-}BuAlMe_2)]$	or	Pbca	8	1806.3(7) 1844.6(8) 2500.3(7)		MnC_5HP	OC[b] 179.9(15,26) C 217.5(12) C 245(2) H 191(12) P 237.6(3)	87.0(6,2.4) d	349
$(n^5\text{-cp}^*)(CO)_2Mn(SiCl_3)_2$	m	$P2_1/c$	4	1203.2(6) 1134.4(5) 1182.2(7)	93.63(4)	MnC_7Si_2	OC 180.7(7,1) (n^5)C 211.3-216.5(6) Si 232.3(2,3)	111.9(3) e	311
$[\{(n^5\text{-cp})_2(CO)Nb\}_2(\mu\text{-H})].[Mn(CO)_5]$	or	$P2_12_12_1$	4	1358.3(3) 1556.5(3) 1262.2(2)		MnC_5	OC not given		350
$[\{(CO)_5Cr\}_2(\mu_3\text{-As})Mn(CO)_5]$[f]	tr	$P\bar{1}$	2	944(1) 972(1) 1334(2)	101.3(1) 96.9(1) 70.1(1)	MnC_5As	OC not given As 251.1(4)		306
$[\{(n^5\text{-cp})Cr(SCMe_3)\}_2(\mu_3\text{-S}).Mn(CO)_2(n^5\text{-cp})$[g]	m	$P2_1/a$	4	1041.4(7) 1351.3(3) 1630.2(9)		MnC_7S	OC 176.0(7,6) (n^5)C 216.3(7) S[c] 233.4(2)	g	351
$[\{(n^5\text{-cp})(CO)Co\}_2(\mu_3\text{-}PCH_2C_6H_5).Mn(CO)_2(n^5\text{-cp})]$[h]	m	$P2_1/c$	4	957.9 1433.8 1765.0	99.08	MnC_7P	OC 174(2,2) (n^5)C 216(2,5) P[c] 224.6(3)	90.5(6) h	352
$(n^5\text{-cp}^*)MnCo_2(n^5\text{-}C_5Me_5)_2(\mu\text{-CO}).(\mu_3\text{-CO})$	m	$P2_1/n$	4	1090.3(4) 1460.5(5) 1724.1(4)	94.42(3)	MnC_8Co_2	(n^5)C[c] - OC[c] Co 256.1		353
$\{\{(CO)_3Co\}_2(\mu_2\text{-}C{\equiv}CPh)Mn(CO)_4.(PCy_3)\}$	m	$P2_1/c$	4	1354.5(5) 1869.1(7) 1694.4(9)	110.89(3)	MnC_5P	OC not given C[c] 206.3(7) P 236.2(3)	not given	354
$(n^5\text{-cp})_2Co_2(\mu_3\text{-CMe})(\mu_2\text{-CO})_2.Mn(CO)_3$	tr	$P\bar{1}$	4	868.01(13) 1356.54(13) 1503.36(16)	84.327(8) 89.258(10) 77.794(10)	MnC_6Co_2	OC 181.5(3,11) OC[c] 211.6(3,10) MeC[c] 192.2(3) Co 250.7(1,8)	93.8(14,2.23) i	355

Table 16, cont. (2)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	(O)C-Mn-C(O) [°]	Ref
$(CO)_8Fe_2(\mu_2\text{-}CO)_2(\mu_3\text{-}PPh)Mn.(\eta^5\text{-}cp)$	m	C2/c	8	1579(2) 1592(2) 1790(3)	 97.2(1) 	MnC_7PFe_2	$(\eta^5)C^c$ 216(2) OC^c 176(2,0) P^c 222.7(6) Fe 274.7(4,5)	87(1) j	356
$(PPh_3)(CO)_8Fe_2(\mu_3\text{-}PPh)Mn(CO)_2.^k(\eta^5\text{-}cp)$	m	$P2_1/c$	4	1262(2) 1586(2) 1732(2)	 92.99(1) 	MnC_7PFe	OC 180(1,2) $(\eta^5)C^c$ not given P^c 222.3(3) Fe 290.8(4)	87.9(3)	357
$\{(PBu_3)(CO)_3Fe\}_2(\mu_3\text{-}PPh)Mn.^l(CO)_2(\eta^5\text{-}cp)^l$	m	$P2_1$	4	1683(1) 1260(2) 2214(2)	 91.40(6) 	MnC_7P MnC_7P	OC 182(4,3) $(\eta^5)C^c$ not given P^c 229(1) OC 175(3,4) $(\eta^5)C^c$ not given P^c 232(1)	not given	358
$[(\eta^5\text{-}C_5Me_5)Mn(CO)_2H]_2(\mu\text{-}SiH_2)$	rh	F2dd	8	919.9(3) 1391.3(3) 4085.7(9)	90 90 90	MnC_7HSi	OC 172(2,0) $(\eta^5)C$ 213(1,3) H^c not given Si^c 243.4(3)	89.9(10) m	359
$[(\eta^5\text{-}cp^*)Mn(CO)_2]_2(\mu\text{-}Ge)$						MnC_7Ge	OC 178.3(6,5) $(\eta^5)C^c$ 214.0(-,28) Ge^c 220.4(1)	93.0(3) n	360
$Mn_2(CO)_8Ge(CH_3)_2$	m	C2/c	8	874.2(2) 1421.5(4) 2722.1(7)	 95.05(5) 	MnC_5GeMn^l	OC 182.3(9,44) OC^c 209.6(8,59) Ge^c 245.5(2,23) Mn^l 285.4(2)	90.7(4,6.3) 177.2(4,1) o	361
$Ti(n^5\text{-}cp)_2[\sigma\text{-}(\eta^4\text{-}C_5H_4)Mn(CO)_3]_2$	m	C2/c	4	1347.4(2) 808.5(1) 2232.7(3)	 105.08(1) 	MnC_7	OC 178.8(3,20) $(\eta^5)C$ 213.9(2,2)	91.5(2,1.8)	362
$(\eta^5\text{-}cp)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_8$	m	$P2_1/a$	4	1487.2(3) 1075.6(2) 1559.1(2)	 114.04(1) 	MnC_5Mn	OC not given Mn 293.8(1)	94.6 p	363

Table 16, cont. (3)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] ß[°] ɣ[°]	Chromophore	M-L [pm]	(O)C-Mn-C(O) [°]	Ref
						MnC_4HMn	OC not given H 177(5) Mn 293.8(1)		363
$[(\eta^5\text{-cp})(CO)Mn]_2(\mu_3\text{-}SeCH_2)$	m	$p2_1/n$	4	1561.6(6) 1315.2(5) 1599.9(4)	103.95(3)	MnC_7Se	OC not given $(\eta^5)C$ not given Se 237.1(2)	q	364
						MnC_8Se	OC not given $(\eta^5)C_c$ not given C^c 210.4(12) Se 248.8(2)		
$[(\eta^5\text{-cp})(CO)_2Mn(\mu_2\text{-}C{=}CH.COOMe)]_2Mo(CO)_2$	m	C2/c	4	1943.6(5) 803.8(2) 1581.7(4)	98.61(2)	MnC_8Mo	OC 178.9(3,16) $(\eta^5)C_c$ 215.1(3,35) C^c 190.9(2) Mo 296.38(3)	86.4(1) r	316
$[(\eta^5\text{-cp}^*)(CO)_2Mn]_2(\mu_3\text{-}As)Mo.^s(CO)_2(\eta^5\text{-cp})^{**}$	tr	P1	2	809.5(5) 913.6(5) 1735.0(8)	91.52(4) 100.58(4) 69.56(4)	MnC_7AS	OC not given $(\eta^5)C_c$ not given As^c 223.5(1)		365
						MnC_7AsMo	OC 178.9(10,19) $(\eta^5)C$ 215.0(9,19) As 231.9(1) Mo 307.0(1)	s	
$[(\eta^5\text{-cp})Mn(CO)_2PPh_3Hg.^t(OCOCF_3)_2]_2^{tt}$	tr	P1	2	947.2(5) 936.9(7) 1681.3(9)	92.06(5) 103.01(4) 91.59(5)	MnC_7PHg	OC 183(2,0) $(\eta^5)C$ 217(2,2) P 230.6(4) Hg 260.2(2)	109.3(6) t	366
$\{(\eta^5\text{-cp})Cr(SCMe_3)\}_2S.Mn_2(CO)_8^{\ddagger}$	m	$P2_1/n$	8	3282.3(4) 1218.4(20) 1745.3(4)	97.55	MnC_5Mn	OC 176(4) Mn 295.3(8)	not given	367
						MnC_4SMn	OC_c 182(5) S^c 244.8(9)		

Table 16, cont. (4)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]		(O)C-Mn-C(O) [°]	Ref
$[(\eta^5\text{-cp})Mn(CO)_2(PMe_2S)Re(CO)_4]_2$	m	$P2_1/c$	2	1131.5 1171.5 1337.2	 91.62 	MnC_7P	OC (η^5)C P	- - -	-	368
$[\{(\eta^5\text{-cp})Mn(CO)_2\}_2\{PFe(CO)_3\}_2]$		supplementary data				MnC_7				369
$\{[(\eta^5\text{-}C_5Me_5)Yb(\mu\text{-}OC)_2Mn(CO)_3]_2\}_n$	m	C2/m	16	1894.2(5) 3259.2(5) 1902.9(5)	 109.92(2) 	MnC_5	OC OC[c]	182.4(8,19) 176.6(7,31)	89.6(3,2.6) 120.0(3,5.8) 175.3(3,4)	370
$[Mn(CO)_4(COCH_3)_2]_3Al$	m	$P2_1/n$	4	1394.8(5) 1218.2(6) 1954.5(6)	 90.51(2) 	MnC_6	OC C	183.9(11,21) 181.8(10)	89.4(6,3.6) 165.4(6)	371
$[(\eta^5\text{-cp}^*)Mn(CO)_2]_3Ge$	m	$P2_1/n$	4	901.5(5) 3060.4(3) 919.9(12)	 107.37(3) 	MnC_7Ge	OC (η^5)C Ge	178.0(-,14) 214.1(-,36) 226.0(2)	91.0(4) v_1	360
						MnC_7GeMn (2x)	OC (η^5)C Ge Mn	178.0(-,14) 214.1(-,36) 237.0(2,11) 298.2(2)	87.9(5,1) v_2	
$[(\eta^5\text{-cp})Mn(CO)_2]_3(\mu_3\text{-}SbCl)$	m	$P2_1/c$	4	1505.2 1243.3 1210.5	 109.1 	MnC_7Sb	OC (η^5)C Sb	not given 212.7(15) 246.3(3)	x	372
						MnC_7SbMn (2x)	OC (η^5)C Sb Mn	not given 213.8(15) 255.4(2,19) 304.3(3)		
$[(\eta^5\text{-cp})Mn(CO)_2]_3(\mu_3\text{-Te})$	m	$P2_1/c$	4			MnC_7Te	OC (η^5)C TC	supplementary data		373

Table 16, cont. (5)

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	Chromophore	M-L [pm]	(O)C-Mn-C(O) [°]	Ref
$[(\eta^5\text{-cp})Mn(CO)_2]_3(\mu_2\text{-}SbCl_2)_2$	tr	P1	1	710.6 756.98 1395.9	96.7 99.3 110	MnC_7Sb_2	OC 178(4,2) (η^5)C 214.0(30) Sb 262.0(4,21)	112.1(14) Y	372
						MnC_7Sb (2x)	OC 176(3,2) (η^5)C 212.0(4) Sb 242.3(4,11)	92.5(14,2)	
$[(\eta^5\text{-cp})MnOs_3(\mu_2\text{-}CH{=}CHPh(\mu\text{-}H)\cdot(\mu\text{-}CO)(CO)_{11}]$	m	$P2_1/c$	4	899.8(1) 1249.1(4) 3208.8(8)	96.55(2)	MnC_9Os	OC 170(3) OC^c 189(3) $(\eta^5)C_c$ 217(4,5) C^c 218(3,10) Os 276.5(4)	z_1	374
$[(\eta^5\text{-cp}^*)_2Cr_2(\mu\text{-}SCMe_3)\cdot(\mu_3\text{-}S)_2Mn^{II}]$	m	Cc	4	2554.0(10) 920.8(3) 2159.5(9)	135.30(2)	MnS_4Cr_4	S^c 240.8(6,94) Cr 298.2(4,143)	z_2	375
$[(\eta^5\text{-cp})_2Cr_2(\mu\text{-}SCMe_3)\cdot(\mu_3\text{-}S)_2]_2Mn^{II}$	or	Fdd2	8	3971.5(13) 2112.7(7) 780.8(3)		MnS_4Cr_4	S^c 239.1(5,2) Cr 294.2(3,6)	z_3	376
$[\{(\eta^5\text{-cp})(CO)_2Mn\}_2BiCl]_2^k$	m	$P2_1/c$	4	1157.3 1330.3 1152.8	116.7	MnC_7Bi	OC 178.3(30) $(\eta^5)C_c$ 215.1(60) Bi^c 246.9(6,2)	z_4	377
$[(\eta^5\text{-cp}^*)Mn(CO)_2Hg]_4$	tg	$I\bar{4}$	2	1595.9(2) 1595.9(2) 768.3(1)		MnC_7Hg_2	OC 178(8,2) $(\eta^5)C_c$ 212(7,6) Hg^c 264.0(7)	87(3) z_5	378
$Ge\{(\eta^5\text{-cp}^*)Mn(CO)_2[Fe(CO)_4]_3\}$	m	Pc	4	970.4(2) 1193.2(3) 2090.1(4)	99.32(2)	MnC_7GeFe	OC not given $(\eta^5)C_c$ not given Ge^c 243.1(1) Fe 286.5(1)	z_6	379
$(\eta^5\text{-}C_5Me_5)MnFe_2Te(CO)_8^{Z_7}$	m	$P2_1/n$	4	982.4(2) 1483.6(3) 1535.5(5)	97.22(2)	MnC_7Fe_2Te	OC 181.5(5,2) (η^5)C 217.3(5,35) Fe 274.0(2,4) Te 251.8(1)	z_7	380

Table 16, Footnotes

a The mean value for chemically identical angle or distance. The first number in parenthesis is the e.s.d. and the second is the maximum deviation from the mean.
b The chemical identity of coordinated atom or ligand.
c The bridge atom (ligand).
d (O)C-Mn-C = 93.2(5,5.0) and 175.8(5,4)°; (O)C-Mn-P = 90.5(4,1.3) and 173.1(4)°; (O)C-Mn-H = 83(4,1) and 168(3); (O)C-Mn-Al = 122.8(4,1.5) and 135.5(4)°; C-Mn-P = 89.2(4,6)°; C-Mn-H = 16(3) and 103(3)°; C-Mn-Al = 41.8(4) and 58.9(3)°; C-Mn-C = 87.9(5)°; Al-Mn-H = 57(3); and P-Mn-Al = 61.8(1) and P-Mn-H = 94(4)°.
e (O)C-Mn-Si = 76.1(2,1.3)°; Si-Mn-Si = 129.05(8)°.
f At 241K.
g At 153K; (O)C-Mn-S = 98.4(2,4)°; S-Mn-cp = 117.5°.
h At 173K; (O)C-Mn-P = 85.2(5) and 95.6(5)°.
i (O)C-Mn-O(C)^{c} = 82.87(13,41), 96.45(12,32) and 172.24(12,1)°; (O)C-Mn-C^{c} = 88.74(12,1.28) and 175.70(13)°; C^{c}-Mn-C^{c} = 76.18(10)°; C^{c}-Mn-C(O)^{c} = 93.84(11,18)°; Co-Mn-C^{c} = 45.77(8,15) and Co-Mn-C(O)^{c} = 48.19(8,5)°.
j Fe-Mn-Fe = 58.5(1)°.
k At 193K.
l There are two crystallographically independent molecules.
m (O)C-Mn-Si = 74.4(5) and 109.5(6)°; Mn-Si-Mn = 124.4(3)°.
n (O)C-Mn-Ge = 90.7(2,3)°; (cp)C-Mn-C(cp) = 38.6(2,5).
o Mn-C-Mn = 85.8(3)°; Mn-Ge-Mn = 71.13(5)°.
p Mn-H-Ta = 138.2(3)°.
q Mn-Se-Mn = 121.5(1)°; Se-Mn-C^{c} = 48.0(3)°.
r (O)C-Mn-C^{c} = 78.0(1) and 108.6(1)°; (O)C-Mn-Mo = 78.63(8) and 109.13(8)°; (O)C-Mn-Cp = 122.4(-,2)°; C^{c}-Mn-Mo = 45.18(7)°; C^{c}-Mn-Cp = 124.6°; Mo-Mn-Cp = 124.1°; Mn-C^{c}-Mo = 94.9(1)°.
s At 230K; Mo-Mn-As = 50.84(3)°; Mn-As-Mn = 135.27(6)°.
t At 153K; (O)C-Mn-P = 82.2(5,5)°; (O)C-Mn-Hg = 71.6(4,1.9)°; P-Mn-Hg = 133.2(1)°.
u (O)C-Mn-C(O)^{c} = 91.0(3,1.0) and 122.1(3,3.5)°; (O)C^{c}-Mn-C(O)^{c} = 116.0(3)°.
v_1 (O)C-Mn-Fe = 90.2(3,4)°;
v_2 (O)C-Mn-Ge = 80.0(3,1.3) and 119.0(4,1.1)°; Mn-Ge-Mn = 78.0(0) and 141.0(1,1.3)°; Mn-Mn-C = 76.0(3,2.1) and 104.8(3,3)°; Mn-Mn-Ge = 51.0(0,3)°.
x Mn-Sb-Mn = 73.0(1), 130.6(1,10.1)°.
y (O)C-Mn-Sb = 77.7(10,3.2), Sb-Mn-Sb = 135.2(1)°; Mn-Sb-Mn = 132.0(1,1.7)°.
z_1 (O)C-Mn-C(O)^{c} = 81.1(1)°; (O)C-Mn-Os = 104(1)°; (O)C-Mn-C^{c} = 78(1) and 111(1)°; (O)C-Mn-Cp = 122°; (O)C^{c}-Mn-Os = 51.3(8)°; (O)C^{c}-Mn-C^{c} = 100(1) and 115(1)°; (O)C^{c}-Mn-cp = 116°; C^{c}-Mn-Os = 49.2(7) and 75.5(6)°; C^{c}-Mn-Cp = 119 and 128°; C^{c}-Mn-C^{c} = 38.8(9)°; Os-Mn-Cp = 131.2°.
z_2 Cr-Mn-Cr = 53.7(1,2.4) and 143.2(1,8.9)°; Cr-Mn-S = 48.0(2,1.3), 110.9(2,3.3) and 162.5(2,2.0)°; Cr-Mn-S(L) = 51.3(2,9), 110.5(2,8) and 157.4(2,1.0)°; S-Mn-S = 84.2(2)°; S-Mn-S(L) = 111.9(2,1.9) and 132.5(2,3.6)°, (L)S-Mn-S(L) = 89.9(2)°.
z_3 Cr-Mn-Cr = 54.41(8) and 143.8(1,5.6)°; Cr-Mn-S = 50.2(1,3), 109.3(1,2.3) and 162.0(1,2.6)°; S-Mn-S = 87.9(2), 114.8(2,2.0) and 128.1(2)°.
z_4 Mn-Bi-Mn = 141.0(2)°.
z_5 (O)C-Mn-Hg = 74(2)°; Hg-Mn-Hg = 66.2(2)°; Mn-Hg-Mn = 157.2°.
z_6 Fe-Mn-Ge = 53.0°; Mn-Ge-Fe = 54.2, 72.9 and 133.7(-,1.0)°.
z_7 At 238K. (O)C-Mn-Fe = 57.0(2,2)°; Te-Mn-Fe = 56.0(0,1)°; Fe-Mn-Fe = 58.5(0)°; Mn-Fe-Te = 57.5(0,0)°; Mn-Fe-Fe = 60.7 (0,2)°; Mn-Te-Fe = 66.6(0,2)°.

found. In these brownish-black prisms, binuclear fragments with Mn and Cr are linked through a η^1-sulphide bridge (Mn-S = 244.8(9)pm, Cr-S-Mn angle = 125.4(5))°. The shortest Mn-M distance is found for Mn-Hg at 260.2(2)pm [366].

Mn_3M units are present in three examples, M = AI [371], M = Ge [360], M = Sb [372] and M = Te [373]. In the pale yellow hexagonal needles of the aluminum derivative [371] the central atom is in fact the aluminum, and the manganese atoms are part of the ligand system around this atom. In the dark red germanium derivative, there is a Ge=$Mn(CO)_2$cp moiety (Mn-Ge = 226.0(2)pm) and a $cp(CO)_2$-Mn-$Mn(CO)_2$cp unit (Mn-Mn = 298.2(2)pm), which is attached to the germanium through two Mn-Ge bonds (235.9(2) and 238.0(1)pm) forming a Mn_2Ge ring. A similar pattern is found in the green Mn_3Sb compound [372] which has a Mn-Mn distance of 304.3(3)pm and two Mn-Sb bonds of 254.0(2) and 257.7(2)pm forming a Mn_2Sb ring.

In another derivative, three $Mn(CO)_2$ cp moieties are held together by a Te atom (mean Mn-Te = 248.5pm) [373].

The only hetero-tetrametallic compound [374] has a metal framework which consists of an osmium triangle with a manganese linked to one corner (Mn-Os = 276.5(4) pm.

The molecular structure of a dark green hetero-pentametallic compound is shown in Figure 23 [375]. The molecule contains a metallospirane core, Cr_4Mn which is strongly distorted in comparison to its cyclopentadienyl analogue [376].

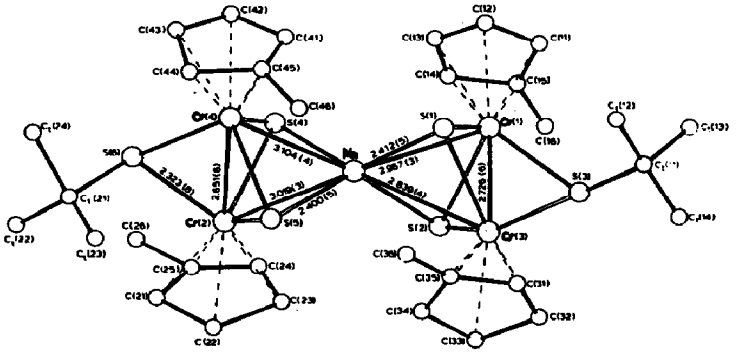

Figure 23. Structure of $[(\eta^5\text{-cp}^*)_2Cr_2(\mu\text{-SCMe}_3(\mu_3\text{-S})_2]_2Mn$
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Table 17 Summary of the manganese-atom (ligand) and rhenium-atom (ligand) distances of carbonyl compounds[a]

Coord. Atom (ligand)	Central Atom	Mononuclear [pm]	Binuclear [pm]	Trinuclear [pm]
H	Mn	146 - 160 (152)	163 - 186 (172)[b]	1.61 - 179 (172)[b]
	Re		170 - 210 (186)[b]	170 - 191 (181)[b]
LH	Mn	164 - 183 (174)		
F	Mn			193 - 197 (195)[b]
	Re	197.0 - 203.9 (200.5)		
LO	Mn	203.1 - 204.2 (203.7)	210.0 235.0 - 235.2 (235.1)[b]	194.0 - 210.0 (202.3)[b]
	Re	218.8 - 223.0 (220.6)	212.9 - 222.0 (214.9)[b] 207.0 - 217.7 (212.5)[b]	217 - 218 (217.5)[b] 212 - 218 (214.5)[b]
LN	Mn	173.0 - 211.0 (201.6)	202.3 - 211.5 (205.6)[b] 197.2 - 211.0 (204.4)[b]	187.9 - 206.1 (196.8)
	Re	176.0 - 235.0 (220.4)	203.0 - 218.0 (210.5)[b] 208.0 - 240.7 (223.2)[b]	209 - 222 (215)
OC	Mn	170.1 - 200.0 (180.5)	166.0 - 189.6 (181.0)[b] 193.0 - 217.3 (200.0)[b]	153.0 - 206.1 (180.1)
	Re	181.0 - 211.0 (192.8)	151.9 - 223.0 (191.1)[b] 192.0 - 214.0 (204.8)[b]	165 - 220 (192) 211.0 - 213.5 (212.6)[b]
LC	Mn	186.2 - 204.7 (196.7)	193.2 - 226.4 (212.5)[b] 205.3 - 210.2 (207.0)[b]	216.1 - 221.7 (218.5)
	Re	193.0 - 212.6 (206.8)	202.7 - 212.7 (205.7)	

Table 17, cont.

Coord. Atom (ligand)	Central Atom	Mononuclear [pm]	Binuclear [pm]	Trinuclear [pm]
S	Mn		241.4 - 244.1 (242.7)	
	Re			252 - 254 (253)[b]
LS	Mn	235.1 - 241.0 (238.3)	222.4 - 240.5 (232.9)[b]	
	Re	243.3 - 253.2 (249.7)	254.1 - 258.6 (255.4)[b]	238.0 - 250.2 (249.8)[b]
LP	Mn	222.2 - 239.8 (227.4)	216.9 - 257.3 (228.3)[b] 225.3 - 236.9 (229.4)[b]	216.1 - 229.0 (228.4)
	Re	241.0 - 253.0 (243.5)	246.0 - 248.5 (246.8)	234.7 - 242.0 (238.0)
Cl	Mn	235.8 - 241.5 (237.6)	237.1 239.4 - 239.9 (239.6)[b]	
	Re	251.5	240.7 - 242.1 (241.6)[b] 244.8 - 253.4 (250.0)[b]	249.3 - 250.2 (249.8)[b]
Br	Mn	250.0 - 255.7 (253.0)	247.7 - 253.4 (251.0)[b]	
	Re	255.1 - 263.6 (261.1)	257.8 - 267.9 (263.6)[b]	
LAs	Mn	243.2	238.6 - 246.0 (240.8) 246.2 - 250.2 (248.2)	
	Re		256.9 - 258.4 (257.5)	
I	Mn			268.9 - 289.2 (279.1)[b]
	Re	277.9	281.3 - 282.7 (282.0)[b]	283.9 271.4 - 284.1 (278.6)[b]

a The mean value is in parenthesis.
b Bridging atom.

Table 18 Summary of the manganese-atom (ligand) and rhenium-atom (ligand) distances of organometallics[a]

Coord. Atom (ligand)	Central Atom	Mononuclear [pm]	Binuclear [pm]	Trinuclear [pm]
ON	Mn	164.7 - 164.7 (166.0)	165.1 - 167.4(165.8) 1.752 - 1.944 (1.854)[b]	184.0 - 186.0 (185.5)[b] 187.3 - 193.8 (190.1)[c]
	Re	169.6 - 180.0 (176.1)		
LN	Mn	169.3 - 206.3 (185.0)	199.2 - 233.4 (218.7) 178.2 - 216.0 (192.7)	187.2[c]
	Re	224.7 - 241.5 (234.3)		
OC	Mn	147.0 - 223.1 (180.0)	170.0 - 185.9 (178.5) 181.0 - 234.0 (206.7)[b]	161.0 - 187.0 (175.8)
	Re	172.0 - 203.1 (192.7)	180 - 208 (194) 208.4 - 222.8 (211.9)[b]	190.0 - 201.2 (195.5)
LC	Mn	168.0 - 230.0 (206.0)	202.6 - 217.7 (212.7)	
	Re	174.2 - 236.0 (216.2)	192.6 - 235.3 (215.9)	205.4 - 244.0 (216.0) 193.0 - 244.7 (225.5)[b]
LC-n^5	Mn	209.7 - 261.4 (230.9)	192.9 - 227.6 (213.7)	213.7 - 217.6 (215.1)
	Re	216.0 - 241.0 (228.1)	224 - 240 (231.5)	222.4 - 236.7 (229.0)
Cl	Mn	235.4	241.1 - 270.1 (251.8)	
	Re		236.0 - 257.8 (247.3)	228.6 - 242.7 (233.1) 238.4 - 245.4 (241.0)[b]
LP	Mn	217.4 - 245.1 (230.0)	228.7 - 268.4 (249.4)[b] 217.8 - 221.6 (219.0)[b]	
	Re	233.7 - 248.1 (240.8)		241.9 - 261.7 (253.8)
I	Mn	264.5		272.2
	Re	269.1 - 277.3 (275.5)	281.3 - 282.7 (282.0)[b]	

a The mean value is in parenthesis; b Doubly bridging atom; c Triply bridging atom.

Table 19 Summary of the metal-metal bond distances[a]

M-M (Oxid. Number)	Bond Distance [pm]	Mean Value [pm]
Re(6) - Re(6)		255.9
Re(5) - Re(5)	255.7, 265.1	260.4
Re(4.33) - Re(4.33)		241.5
Mn(4) - Mn(4)	282.0 - 294.3	288.2
Tc(4) - Tc(4)	233.1 - 236.3	234.7
Re(4) - Re(4)	236.2 - 286.5	267.5
Re(3.84) - Re(3.84)	279.3 - 292.2	285.5
Re(3.5) - Re(3.5)		
Mn(3) - Mn(3)	272.0 - 286.9	277.3
Tc(3) - Tc(3)	213.3 - 219.2	215.5
Re(3) - Re(3)	216.9 - 296.0	257.3
Tc(2.66) - Tc(2.66)	241 - 260	250
Tc(2.5) - Tc(2.5)	209.5 - 212.6	211.3
Re(2.5) - Re(2.5)	222.9 - 268.3	239.2
Mn(2) - Mn(2)	251.6 - 284.1	275.0
Re(2) - Re(2)	221.1 - 258.6	230.1
Tc(1.83) - Tc(1.83)	216 - 270	
Mn(1) - Mn(1)	250.3 - 298.2	276.6
Tc(1) - Tc(1)	253.1 - 272.1	264.4
Re(1) - Re(1)	281.6 - 295.0	288.6
Mn(0) - Mn(0)	217.0 - 297.7	271.4
Re(0) - Re(0)	241.1 - 295.7	281.5
Mn(4) - Mn(3)	271.6 - 276.3	274.0
Mn(2) - Mn(0)	252.0, 252.6	252.3
Re(5) - Re(4)		250.8
Re(5) - Re(1)		238.1
Re(4) - Re(2)	223.1 - 261.3	242.2
Re(3) - Re(2)	229.0 - 242.1	237.1

a Only distances smaller than 300 PM are tabulated. Data for Tc-Tc and Re-Re bond distances are taken from references [381, 382].

A black Mn/Hg derivative [378] has an eight-membered Mn_4Hg_4 ring. The four Hg atoms are almost coplanar (deviation 0.4pm), while the four Mn atoms are 35.9 pm out of plane from each other. The non-linearity of the Mn-Hg-Mn groups (157.2°) indicates metal-metal interaction (Mn-Hg = 264.0pm).

Finally, there are two examples [379,380] in which three different metal atoms are present (Table 16).

4. SUMMARY

The manganese carbonyl compounds are found with coordination numbers from four to six, the latter being the most common. Several derivatives exist as isomers (13,14,26,35,103), and independent molecules exhibiting distortion isomers have also been noted (7,10,38,50).

The most common structures are mono-, bi- and polynuclear, with a few examples of tri-, tetra- and hexanuclearity.

A summary of the M-L bond distances for the mono-, bi- and trinuclear carbonyls is given in Table 17. The data for the rhenium compounds are from an earlier review (4). The following general observations can be made:

(a) The Mn-L bond distances are shorter than those for Re-L.

(b) The M-L bond distances elongate with the van der Waals radius of the coordinating atom.

The nearly 300 manganese organometallic compounds reviewed here are mostly mono- and bimetallic with a few examples up to pentametallic.

Distortion isomerism has been found in 14 examples:
(161, 199, 200, 229, 231, 232, 237, 291, 316, 334, 338, 348, 358, 367)

The cyclopentadienyl ring is by far the most common ligand, and a tetragonal arrangement about the metal is the preferred molecular geometry. Binuclear manganese compounds with two linking ligands are the most common bridging structure encountered.

A summary of the structural data for organometallic manganese and rhenium [4] compounds is given in Table 18, from which the following general observations can be made:

(a) The mean Mn-L bond distance is somewhat shorter than that for rhenium.

(b) The mean Mn-L (bridge) bond distance is longer than the mean M-L (terminal) value, except in the case of Mn-P.

(c) The M-L bond distances increase with increasing van der Waals radius of the ligated atom.

A summary of metal-metal bond distances is given in Table 19, and includes data for the compounds in this review, manganese coordination compounds (383), rhenium compounds (4,382) and technetium compounds (381). The following general observations can be made:

(a) Metal-metal bonding chemistry for manganese shows less variety than that of rhenium.

(b) Non-integer oxidation states are not involved for manganese contrary to the case for technetium or rhenium.

(c) At higher oxidation states (+2 to +4) manganese bonds are longer than those of rhenium, while at lower oxidation states (0,+1) the reverse is true.

(d) Technetium metal-metal bonds tend to be shorter than those of either manganese or rhenium.

There is also a rich variety of heterometallic compounds with a direct Mn-M bond. The mean values of these bonds increases in the order shown below:
(Mn-Ge) 242.7pm <(-Ga) 245.0pm <(-Bi) 246.9pm <(-Co) 250.2pm
<(-Hg) 254.2pm <(-In) 264.0pm <(-Li) 264.5pm <(-Sn) 266.6pm
<(-Pt) 270.0pm <(-Cd) 271.4pm <(-Fe) 274.4pm <(-Rh) 275.5pm
<(-Pd) 281.1pm <(-Mo) 287.3pm <(-Re) 292.7pm <(-Cr) 296.2pm
<(-W) 299.4pm

Despite the variety of the compounds discussed above, many systematic trends are observable, and this review attempts to document and clarify these. It is anticipated that these observations may suggest directions that might be fruitful for further investigation.

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