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PREPARATION OF HETEROMETALLIC COMPLEXES WITH CHELATING μ_2-CARBOMETHOXYVINYLIDENE LIGANDS. X-RAY CRYSTAL STRUCTURES OF $Cp(OC)_2MnW(CO)_4(\mu$-C=CHCOOMe) AND $[Cp(OC)_2Mn(\mu_2$-C=CHCOOMe$)]_2Mo(CO)_2$ (Cp = η^5-C_5H_5)

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Summary

$Cp(OC)_2Mn$=C=$CHCO_2Me$ and $Cp(OC)_2Mn(\eta^2$-HC≡$CCO_2Me)$ react with $M(CO)_5(THF)$ (M = Mo, W) yielding the heterometallic complexes $Cp(OC)_2$-$MnM(CO)_4(\mu$-C=CHCOOMe) (VIa: M = W, VIb: M = Mo) and $[Cp(OC)_2$-$Mn(\mu_2$-C=CHCOOMe$)]_2Mo(CO)_2$ (VII). VIa and VIb have Mn–W and Mn–Mo bonds and VII has two Mn–Mo bonds bridged by the carbomethoxyvinylidene ligand, chelating Mo or W by carbonyl oxygen. VIa and VII have been characterized by an X-ray diffraction study.

Introduction

Mononuclear complexes with unsaturated carbene, viz. vinylidene or allenylidene, ligands can give species with metal–metal bonds bridged via the terminal atom of a carbene moiety. The first example reported was the reaction between $Cp(OC)_2M$=C=CHPh and $Cp(OC)_2M'(THF)$ (M and M' = Mn, Re), yielding binuclear $Cp_2(OC)_4MM'(\mu$-C=CHPh) complexes with the Mn–Mn, Mn–Re or Re–Re bond bridged by a phenylvinylidene ligand [1–3]. Later, Berke [4] and we [5] studied similar reactions of $Cp(OC)_2Mn$=C=$CHCO_2Me$ (I) and allenylidene manganese complexes [6] and prepared $[Cp(OC)_2Mn]_2(\mu$-C=$CHCO_2Me)$ (II) and $[Cp(OC)_2Mn]_2(\mu$-C=C=$CR_2)$ (R = Ph, t-Bu, cyclohexyl, CH_2Ph), respectively.

The manganese vinylidene complexes $Cp(OC)_2Mn$=C=CHR react with $Fe_2(CO)_9$ similarly. The structure of the product depends on the nature of the substituent R. If R = Ph, complex III with a manganatrimethylenemethane moiety π-bonded to iron is formed [7]. On the contrary, under the same conditions, I (R = CO_2Me) gives the heterometallic complex IV, the *E* and *Z* isomers of which were isolated [8].

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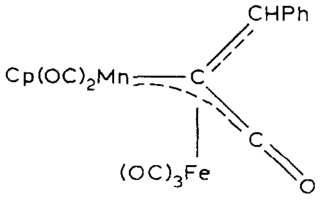

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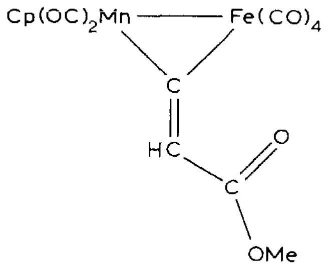
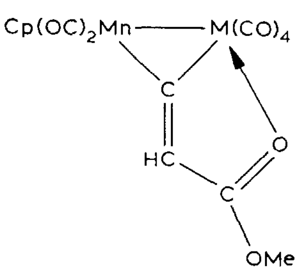
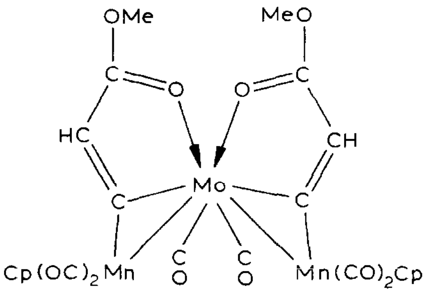


(Z-IV)



(VIa: M = W;
VIb: M = Mo)



(VII)

In the present paper we report the reactions of I and $Cp(OC)_2Mn(\eta^2$-$HC{\equiv}CCO_2Me)$ (V) with Group VI metal carbonyl derivatives, $M(CO)_5(THF)$ (M = Cr, Mo and W).

Results and discussion

I and V react with $W(CO)_5(THF)$ in THF at 60°C, yielding the heterometallic complex VIa with a Mn–W bond bridged by the carbomethoxyvinylidene ligand chelating the tungsten atom by its carbonyl oxygen. With $Mo(CO)_5(THF)$, under the same conditions, I forms complex VIb (isostructural and isoelectronic with VIa) and a trinuclear complex VII, while V gives VII as a single product. In VII the Mo atom participates in two Mn–Mo bonds bridged by μ_2-carbomethoxyvinylidene moieties chelating Mo in the same manner as W in VI.

$Cr(CO)_5(THF)$ does not react with I and V under mild conditions.

VI and VII are dark brown, crystalline, air-stable substances, moderately soluble in aliphatic hydrocarbons and CCl_4 but readily soluble in CH_2Cl_2, $CHCl_3$ and polar solvents.

The IR spectra (Table 1) of VIb, on one hand, and of VIa and VII, on the other, exhibit respectively five and six $\nu(C{\equiv}O)$ bands in the range 1800–2100 cm^{-1}, corresponding to terminal carbonyl groups. The frequencies and relative intensities of these bands are similar for VIa and VIb, proving them to be isostructural. The spectrum of VII differs from that of VI by the absence of a $\nu(C{\equiv}O)$ band at 2060 cm^{-1} and the presence of another one at 1870 cm^{-1}. It is noteworthy that neither VI nor VII exhibits ν(C=O) bands at 1700–1720 cm^{-1} characteristic of the CO_2Me group. Nevertheless, the intense bands at about 1550 cm^{-1} can be attributed to this ester group coordinated with Mo or W via its carbonyl oxygen, thus forming a chelate ring (cf. 1514 cm^{-1} for $Cp(OC)_2MoC(Me){=}C(Me)COMe$ [9]).

In the ^1H NMR spectra of VI and VII (Table 1) there are three singlets, viz. at 4.6–4.9 (Cp), 3.33–3.9 (OMe) and 7.04–7.2 ppm (=CH), with an intensity ratio of 5/3/1. The chemical shifts of all of these signals are in agreement with those of I, II [5] and V.

In the ^{13}C NMR spectrum of VIa (Table 1), the signal of the α-carbon atom of the bridging carbomethoxyvinylidene ligand (347.8 ppm) is shifted to lower field with respect to the signals in the spectra of $[Cp(OC)_2Mn]_2(\mu\text{-}C{=}CHPh)$ (VIII) (284.16 ppm) [1] and II (284.41 ppm) [5].

The mass spectra of VIa and VIb exhibit peaks of molecular ions P^+ at m/z 556 (^{184}W) and 470 (^{98}Mo), respectively, and decarbonylated ions $P^+ - n(CO)$ ($n = 1$–6). The mass spectrum of VII could not be measured.

The molecular structures of VIa and VII (Figs. 1 and 2, Tables 2 and 3) were established by an X-ray single-crystal study. Although the crystals of VIa and the Z isomer of IV are not isostructural, their molecular structures are similar. The main difference is caused by the different coordination of the W atom in VIa and the Fe atom in Z-IV, which does not form a bond with O(7). The trinuclear molecule of VII is situated on a crystallographic two-fold axis passing through the Mo atom.

The geometries of the $Cp(OC)_2Mn$ moieties and vinylidene bridges in VIa and VII are essentially the same. Most of the bonds formed by the W atom in VIa are slightly longer than the Mo bonds in VII. However, the O(7)–W and O(7)–Mo bond

TABLE 1

IR AND NMR SPECTRAL DATA

Complex	ν(cm^{-1}, CCl_4)		$\delta(^1H)$ (ppm) TMS				Ref.
	ν(C≡O)	ν(C=O)	Cp	OCH_3	CH	Solvent	
I	2030vs, 1975vs (cyclohexane)	1712s	5.10s	3.61s	5.85s	CCl_4	27
V	2000vs, 1940vs (n-hexane)	1715s	4.73s	3.92s	6.33s	$CDCl_3$	27
VIa	2057vs, 1990vs, 1975m 1958s, 1932vs, 1912w	1550vs	4.94s	3.90s	7.20s	CCl_4	This work
VIb	2060vs, 1990vs, br 1957vs, 1945vs, 1915w broad	1555vs	–	–	–	–	This work
VII	2010w, 1995vw, 1985vs, 1946vs, 1912w, 1870w,br	1550vs	4.66s	3.33s	7.04s	$CDCl_3$	This work

	Cp	CO at Mn	CO at W	C=O	C_α [a]	C_β [a]	CH_3	
VIa	88.27	228.08	222.01 221.07 216.43	186.01	347.80	122.51	53.61	This work

[a] C_α and C_β of the carbomethoxyvinylidene moiety (i.e. C(7) and C(8) in Figs. 1 and 2).

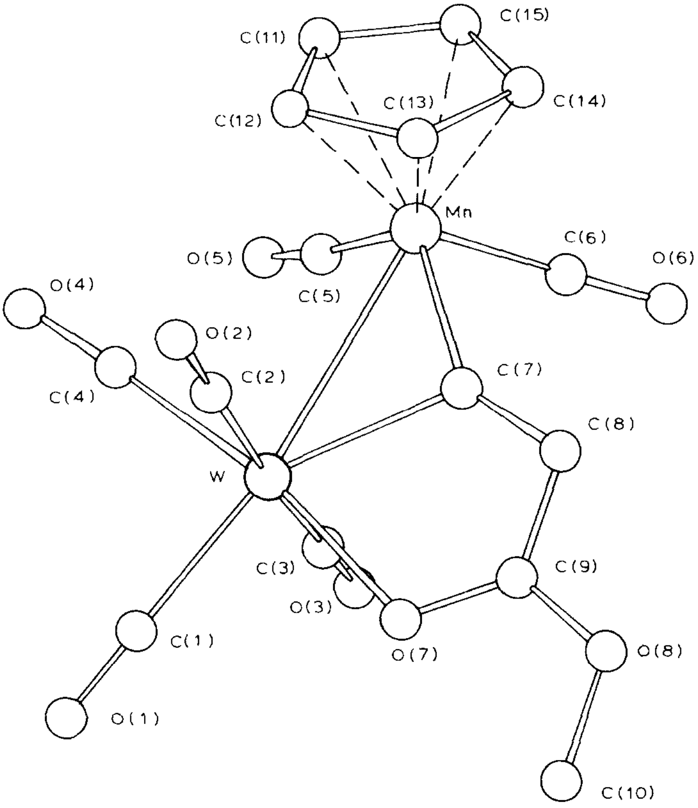


Fig. 1. Molecular structure of VIa (hydrogen atoms have been omitted).

TABLE 2

BOND DISTANCES (Å) IN THE STRUCTURES OF VIa (M = W) AND VII (M = Mo)

Bond	VIa	VII	Bond	VIa	VII
M–Mn	2.9939(8)	2.9638(3)	C(1)–O(1)	1.135(8)	–
M–O(7)	2.238(4)	2.238(2)	C(2)–O(2)	1.151(7)	1.150(3)
M–C(1)	2.050(6)	–	C(3)–O(3)	1.129(7)	–
M–C(2)	1.996(5)	1.976(2)	C(4)–O(4)	1.145(7)	–
M–C(3)	2.051(6)	–	C(5)–O(5)	1.154(7)	1.149(3)
M–C(4)	2.041(6)	–	C(6)–O(6)	1.157(7)	1.150(3)
M–C(7)	2.130(5)	2.110(2)	C(7)–C(8)	1.337(7)	1.346(3)
M...C(5)	3.186(6)	3.151(2)	C(8)–C(9)	1.427(8)	1.432(3)
Mn–C(5)	1.811(6)	1.804(2)	C(9)–O(7)	1.255(6)	1.241(3)
Mn–C(6)	1.773(6)	1.773(3)	C(9)–O(8)	1.322(7)	1.329(3)
Mn–C(7)	1.903(5)	1.909(2)	O(8)–C(10)	1.442(7)	1.450(3)
Mn–C(11)	2.158(6)	2.162(3)	C(11)–C(12)	1.421(8)	1.407(4)
Mn–C(12)	2.171(6)	2.186(3)	C(12)–C(13)	1.411(8)	1.417(4)
Mn–C(13)	2.144(6)	2.153(3)	C(13)–C(14)	1.413(9)	1.410(4)
Mn–C(14)	2.117(6)	2.129(3)	C(14)–C(15)	1.426(9)	1.413(4)
Mn–C(15)	2.126(6)	2.126(3)	C(15)–C(11)	1.391(8)	1.405(4)
Mn–Cp	1.774	1.785			

distances are equal (2.238 Å) and usual for a donor–acceptor bond involved in a 5-membered chelate ring, cf. 2.21–2.24 Å in molybdenum maleate complexes [11], 2.31 and 2.25 Å in two isostructural complexes $(\eta^3\text{-}C_3H_5)(OC)_2M(O_2CCF_3)$-$(MeOCH_2CH_2OMe)$, with M = Mo and W, respectively [12].

According to the EAN rule, the Mn–W (in VIa) and Mn–Mo (in VII) distances correspond to single bonds, which, however, are significantly shortened due to the presence of μ-vinylidene ligands. Thus the Mn–Mo distance in VII is 2.964 vs. 3.08 Å in the unbridged complex $Cp(OC)_3MoMn(CO)_5$ [13] and 3.054 Å in $(C_5H_4PPh_2)(OC)_3MoMn(CO)_4$ [14]. In the latter, the phosphonium ylide coordinating manganese by its P atom and molybdenum by the Cp ring causes no shortening of the Mo–Mn bond.

To our knowledge, VIa is the first organometallic compound with a Mn–W bond studied by X-ray diffraction. This bond is shorter (2.994 Å) than half the sum (3.07 Å) of the single-bonded distances Mn–Mo of 2.904 Å in $Mn_2(CO)_{10}$ [15] and W–W of 3.24 Å in $[Cp(OC)_3W]_2$ [16].

All the carbonyl groups in VIa and VII are terminal, except the semi-bridging C(5)O(5) group. The latter is directed towards the W(Mo) atom (the WMnC(5) angle being acute) and interacts weakly with it. Therefore the Mn–C(5)–O(5) moiety is bent (7.4° in VIa, 8.0° in VII), and the Mn–C(5) bond is 0.03–0.04 Å longer than the Mn–C(6) bond of the terminal CO group. In Z-IV and $[Cp(OC)_2Mn]_2(\mu$-C=CHR) (VIII, R = Ph [17], H [18]), one of the CO groups at the Mn atom is always semi-bridging, as in VIa and VII. In VIa the WC(2)O(2) bond, which is *trans* to O(7), is considerably shorter (1.996 Å) than the other W–CO bonds, which are *trans*

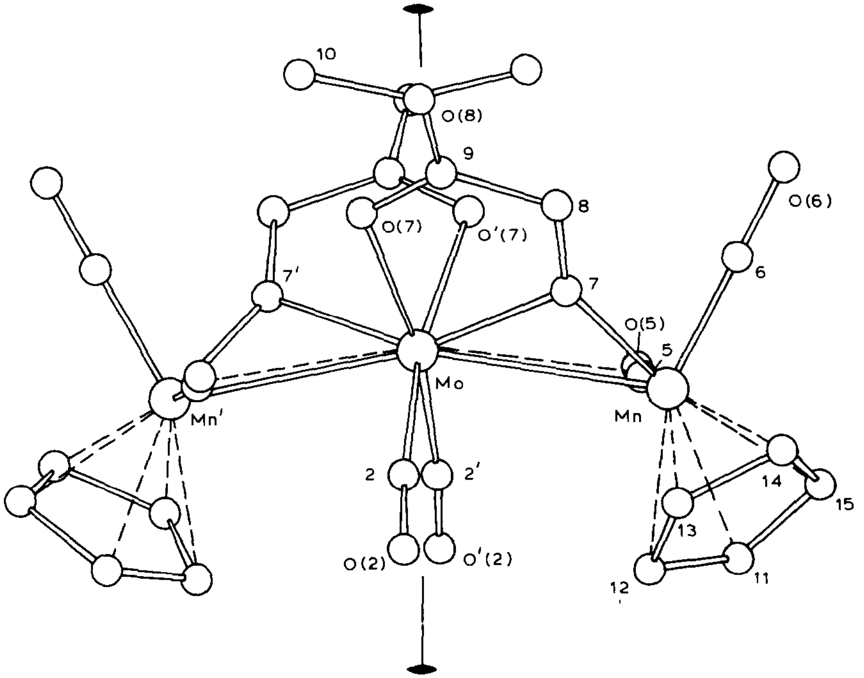


Fig. 2. Molecular structure of VII (projection on the $MoMn_2$ plane; hydrogen atoms have been omitted).

to the CO groups and the μ-vinylidene ligand and have an average length of 2.047 Å.

In both VIa and VII, the W (or Mo), Mn, C(7), C(8), C(9) and O(7) atoms are coplanar within 0.03 (VIa) or 0.04 Å (VII). Their mean plane (A) forms a dihedral angle of 37.2° (VIa) or 38.7° (VII) with the Cp plane. The plane defined by the three metal atoms in VII forms an angle of 66.5° with the A plane and an angle of 44.2° with the Cp plane. The O(8) and C(10) atoms are bent out of the A plane by −0.06 and 0.02 Å in VIa and by 0.17 and 0.29 Å in VII.

In Table 4 the geometrical parameters of the carbomethoxyvinylidene moiety in VIa, VII and Z-IV are compared with the corresponding average values in uncoordi-

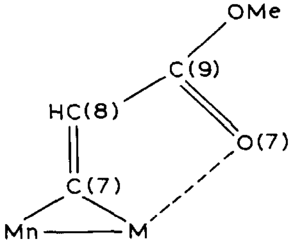
TABLE 3

BOND ANGLES (°) IN THE STRUCTURES OF VIa AND VII

Angle		Angle		Angle	
Structure VIa					
MnWO(7)	111.6(1)	O(7)WC(3)	78.1(2)	C(2)WC(3)	90.9(2)
MnWC(1)	88.5(2)	O(7)WC(4)	90.5(2)	C(2)WC(4)	85.6(2)
MnWC(2)	79.5(2)	O(7)WC(5)	133.9(1)	C(2)WC(5)	110.4(2)
MnWC(3)	170.2(2)	O(7)WC(7)	90.5(2)	C(2)WC(7)	118.6(2)
MnWC(4)	88.5(2)	C(1)WC(2)	92.5(2)	C(3)WC(4)	92.7(2)
MnW · · · C(5)	33.9(1)	C(1)WC(3)	90.0(2)	C(3)WC(5)	66.3(2)
MnWC(7)	39.2(1)	C(1)WC(4)	176.7(2)	C(3)WC(7)	150.5(2)
O(7)WC(1)	91.9(2)	C(1)WC(5)	137.7(2)	C(4)WC(5)	57.8(2)
O(7)WC(2)	168.1(2)	C(1)WC(7)	90.5(2)	C(4)WC(7)	88.1(2)
				C(5)WC(7)	114.6(2)
Structure VII					
MnMoMn′	160.16(1)	O(7)MoO(7)	87.04(5)	C(2)MoC′(5)	57.85(8)
MnMoO(7)	113.02(4)	O(7)MoC(2)	94.34(8)	C(2)MoC(7)	90 0(1)
MnMoO′(7)	81.89(4)	O(7)MoC′(2)	169.27(8)	C(2)MoC′(7)	117.6(1)
MnMoC(2)	87.79(7)	O(7)MoC(5)	130.98(6)	C(5)MoC′(5)	167.48(6)
MnMoC′(2)	77.71(7)	O(7)MoC′(5)	60.16(6)	C(5)MoC(7)	66.57(7)
MnMoC(5)	34.15(4)	O(7)MoC(7)	73.10(7)	C(5)MoC′(7)	117.84(7)
MnMoC(5)	142.19(4)	O(7)MoC′(7)	80.19(7)	C(7)MoC′(7)	142.9(8)
MnMoC(7)	39.92(6)	C(2)MoC′(2)	86.3(1)		
MnMoC′(7)	151.22(6)	C(2)MoC(5)	111.90(8)		
Angle	VIa	VII	Angle	VIa	VII
MMnC(5)	78.9(2)	78.63(8)	MnC(5)O(5)	172.6(5)	172.0(2)
MMnC(6)	107.8(2)	109.13(8)	MnC(6)O(6)	177.7(5)	179.2(2)
MMnC(7)	45.1(2)	45.18(7)	MC(7)Mn	95.7(2)	94.9(1)
MMnCp	125.0	124.1	MC(7)C(8)	119.6(4)	119.3(2)
C(5)MnC(6)	88.5(3)	86.4(1)	MnC(7)C(8)	144.7(4)	145.8(2)
C(5)MnC(7)	113.1(2)	108.6(1)	C(7)C(8)C(9)	112.9(5)	112.4(2)
C(5)MnCp	121.1	122.5	C(8)C(9)O(7)	120.2(5)	121.0(2)
C(6)MnC(7)	80.0(2)	78.0(1)	C(8)C(9)O(8)	118.6(5)	118.1(2)
C(6)MnCp	122.1	122.2	O(7)C(9)O(8)	121.2(5)	120.9(2)
C(7)MnCp	120.5	124.6	MO(7)C(9)	114.8(3)	114.0(1)
MC(1)O(1)	179.0(5)	–	C(9)O(8)C(10)	116.5(4)	114.9(2)
MC(2)O(2)	176.8(5)	175.5(2)	C(12)C(11)C(15)	109.4(5)	108.6(2)
MC(3)O(3)	179.2(5)	–	C(11)C(12)C(13)	107.1(5)	107.3(2)
MC(4)O(4)	175.3(5)	–	C(12)C(13)C(14)	108.1(5)	108.5(2)
M…C(5)Mn	67.2(2)	67.22(7)	C(13)C(14)C(15)	108.1(5)	107.4(2)
M…C(5)O(5)	120.0(4)	120.0(8)	C(14)C(15)C(11)	107.3(5)	108.2(2)

TABLE 4

GEOMETRY OF THE CARBOMETHOXYVINYLIDENE MOIETY IN COMPLEXES VIa, VII, Z-IV AND UNCOORDINATED MOLECULE IX (average)



Structure	VIa	VII	Z-IV	IX
	M = W	M = Mo	M = Fe	–
Distance (Å)				
M–C(7)	2.130(5)	2.110(2)	1.94(1)	–
C(7)–C(8)	1.337(7)	1.346(3)	1.30(2)	1.316
C(8)–C(9)	1.427(8)	1.432(3)	1.49(3)	1.478
C(9)–O(7)	1.255(6)	1.241(3)	1.21(2)	1.188
M–O(7)	2.238(4)	2.238(2)	3.50(1)	–
M–Mn	2.9939(8)	2.9638(3)	2.703(4)	–
Mn–C(7)	1.903(5)	1.909(2)	1.95(1)	–
Angle (°)				
MC(7)C(8)	119.6(4)	119.3(2)	139(1)	–
C(7)C(8)C(9)	112.9(5)	112.4(2)	127(2)	120.8
C(8)C(9)O(7)	120.2(5)	121.0(2)	124(2)	126.1
Torsion angle (°)				
C(7)C(8)C(9)O(7)	2.0(5)	6.0(2)	21	7

nated molecules of *meta*- [19] and *para*-$C_6H_4(CH{=}CHCO_2Me)_2$ [20] and (4-HO)(3-O_2N)$C_6H_3CH{=}CHCO_2Me$ [21] *. In all three complexes the C(7)=C(8) and C(9)=O(7) double bonds have *cis* orientation, as in IX. In Z-IV the O(7) atom is pushed away from the Fe atom with a filled 18-electron shell. The Fe...O(7) distance is increased to 3.50 Å due to widening of the C(7)C(8)C(9) and FeC(7)C(8) bond angles and to the increasing C(7)C(8)C(9)O(7) torsion angle (Table 4). On the contrary, in VIa and VII the carbomethoxyvinylidene ligand is bent towards the W(Mo) atom and the C(7)C(8)C(9) and C(8)C(9)O(7) angles are decreased.

The bond distances in the carbomethoxyvinylidene moiety of Z-IV are essentially the same as those in IX and consistent with the standard geometry of an ester group [22]. In VIa and VII the formation of 5-membered metallacycles leads to some π-delocalization. In VIa and VII the C(8)–C(9) single bond is shorter and both the C(7)=C(8) and C(9)=O(7) double bonds are longer than those in Z-IV and IX, although the C(7)=C(8) bond length in VIa and VII is close to the standard $C(sp^2){=}C(sp^2)$ bond length of 1.333 Å [23], while in Z-IV and IX it is still shorter. The Mn–C(7) bonds in VIa and VII are shorter than those in Z-IV (1.95 Å) and VIII (average 1.97 Å). All these features are consistent with a contribution of the form **1** to the structures of VIa and VII.

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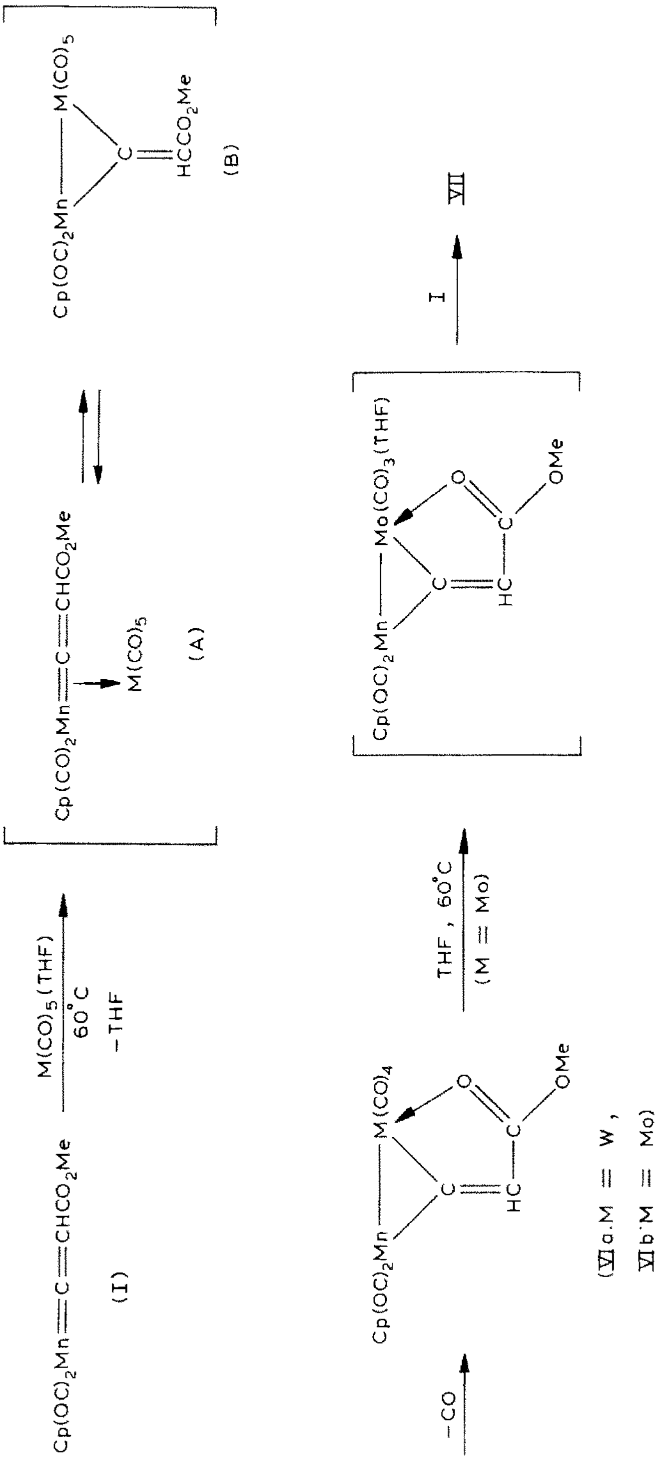
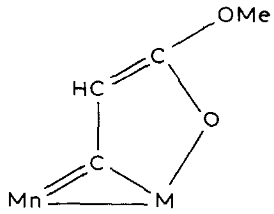
* From here onwards the uncoordinated $MeO_2CCH{=}CH$ group is referred to as IX.


Cp(OC)$_2$Mn=C=CHCO$_2$Me
(I)
M(CO)$_5$(THF)
60°C
−THF
Cp(CO)$_2$Mn=C=CHCO$_2$Me
M(CO)$_5$
(A)
Cp(OC)$_2$Mn—M(CO)$_5$
C
HCCO$_2$Me
(B)
−CO
Cp(OC)$_2$Mn—M(CO)$_4$
C
HC
C
O
OMe
(VIa. M = W,
VIb M = Mo)
THF, 60°C
(M = Mo)
Cp(OC)$_2$Mn—Mo(CO)$_3$(THF)
I
VII

SCHEME 1



(1)

Probably the formation of VI from I and $M(CO)_5(THF)$ (M = Mo, W) proceeds via an intermediate π-complex A and its isomer B (Scheme 1). The latter is unstable due to steric hindrance between one of the carbonyl groups at the M atom and the ester group. The steric strain is released by elimination of the CO group mentioned. The arising electron defficiency of M is then compensated by a lone pair of electrons of the oxygen atom. This replacement is thermodynamically favourable because in the case of Group VI transition metals the $M \leftarrow O{=}C$ bond has a higher dissociation energy than the M–CO bond, e.g. from thermochemical data, 45.4 kcal/mol for $Mo \leftarrow O$(pentane-2,4-dione) vs. 36.2 kcal/mol for Mo–CO. Both bond energies increase in the series $Cr < Mo < W$ [24–26]. The π-delocalization over the metallacycle (see above) in VI and VII can provide an additional energy gain.

The formation of VIa and VII from V is probably preceded by rearrangement (induced by $M(CO)_5(THF)$) of the π-acetylene ligand of V into an η^1-vinylidene ligand.

The reactions of I and V with $W(CO)_5(THF)$ stop at the stage of the formation of VI, while the reactions of the same complexes with $Mo(CO)_5(THF)$ proceed further to the trinuclear bis-chelate complex VII. As the dissociation energy of the M–CO

(Continued on p. 430)

TABLE 5

CRYSTAL DATA

	VIa	VII
Formula	$C_{15}H_9MnO_8W$	$C_{24}H_{18}Mn_2MoO_{10}$
Space group	$P2_1/n$	$C2/c$
a, Å	7.523(3)	19.436(5)
b, Å	19.456(6)	8.038(2)
c, Å	11.175(4)	15.817(4)
β, °	96.04(3)	98.61(2)
V, Å^3	1627(1)	2443(1)
Z	4	4
d_{calcd}, g cm^{-3}	2.27	1.88
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$, °	54	60
No. of independent reflections with $I \geqslant 2\sigma$	2965	2443
R	0.030	0.023
R_w	0.036	0.023
Weighting scheme	$w = [\sigma_F^2 + (0.005\|F_0\|)^2]^{-1}$	$w = \sigma_F^{-2}$
μ(Mo-K_α), cm^{-1}	83.3	15.9

TABLE 6

ATOMIC COORDINATES ($\times 10^4$; for W, Mo and Mn $\times 10^5$) AND ANISOTROPIC THERMAL FACTORS $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Structure VIa									
W	14052(3)	4803(1)	29487(2)	1.10(1)	1.27(1)	1.35(1)	−0.025(6)	0.146(7)	0.021(6)
Mn	24760(10)	19630(4)	30173(7)	1.24(3)	1.32(3)	1.74(3)	−0.03(3)	0.26(2)	−0.12(2)
O(1)	−753(6)	757(2)	387(4)	3.9(2)	2.7(2)	2.2(2)	0.0(2)	−1.1(2)	0.3(2)
O(2)	−1638(5)	1093(2)	4356(4)	2.0(2)	2.3(2)	2.5(2)	0.4(1)	0.8(1)	0.4(1)
O(3)	−354(5)	−1004(2)	3012(4)	2.6(2)	1.9(2)	3.0(2)	−0.4(2)	0.6(1)	−0.2(1)
O(4)	3463(6)	339(2)	5576(4)	2.4(2)	2.8(2)	1.7(2)	0.4(1)	−0.1(1)	0.1(1)
O(5)	−1388(5)	2147(2)	2275(4)	1.5(2)	2.7(2)	2.8(2)	0.6(1)	0.0(1)	0.6(2)
O(6)	3214(5)	2358(2)	558(4)	2.1(2)	3.6(2)	2.5(2)	0.4(2)	0.7(1)	1.0(2)
O(7)	3415(4)	−176(2)	2145(3)	1.4(1)	1.6(2)	1.9(2)	0.0(1)	0.4(1)	−0.2(1)
O(8)	6101(5)	−192(2)	1439(4)	1.8(2)	1.8(2)	2.7(2)	0.3(1)	0.5(1)	0.8(1)
C(1)	22(8)	653(3)	1296(6)	2.0(2)	1.6(2)	2.4(3)	0.2(2)	0.2(2)	0.0(2)
C(2)	−537(7)	883(3)	3815(5)	1.6(2)	1.7(2)	1.8(2)	−0.3(2)	0.4(2)	0.5(2)
C(3)	271(7)	−477(3)	2998(5)	1.5(2)	1.6(2)	2.3(2)	−0.1(2)	0.2(2)	0.1(2)
C(4)	2768(7)	367(3)	4615(5)	1.3(2)	1.7(2)	2.0(2)	0.3(2)	0.4(2)	0.0(2)
C(5)	104(7)	2029(3)	2547(5)	2.3(2)	1.3(2)	1.9(2)	−0.2(2)	0.5(2)	0.2(2)
C(6)	2886(7)	2205(3)	1541(5)	1.1(2)	1.9(2)	2.5(2)	0.2(2)	0.5(2)	0.4(2)
C(7)	3504(7)	1135(3)	2500(5)	1.5(2)	1.5(2)	1.4(2)	−0.3(2)	0.0(2)	0.0(2)
C(8)	4912(7)	864(3)	2034(5)	1.4(2)	1.5(2)	2.0(2)	0.0(2)	0.2(2)	0.0(2)
C(9)	4779(7)	137(3)	1882(5)	1.6(2)	2.0(2)	1.3(2)	−0.3(2)	0.1(2)	−0.1(2)
C(10)	5860(8)	−919(3)	1240(6)	2.4(2)	1.9(2)	3.0(3)	0.1(2)	0.6(2)	−0.6(2)

C(11)	2047(8)	2622(3)	4513(5)	2.3(2)	1.8(2)	2.0(2)	0.0(2)	0.5(2)	−0.5(2)
C(12)	2835(8)	1998(3)	4970(5)	2.7(2)	2.0(2)	1.8(2)	0.0(2)	0.0(2)	−0.6(2)
C(13)	4507(8)	1939(3)	4514(5)	2.1(2)	2.8(3)	1.9(2)	0.0(2)	−0.4(2)	−0.9(2)
C(14)	4735(8)	2518(4)	3782(6)	1.7(2)	3.0(3)	3.1(3)	−0.9(2)	0.3(2)	−1.5(2)
C(15)	3182(8)	2939(3)	3778(5)	2.4(2)	1.8(2)	2.4(2)	−0.3(2)	0.4(2)	−0.6(2)
Structure VII									
Mo	0	10315(3)	1/4	0.948(9)	1.17(1)	0.94(1)	0	−0.017(7)	0
Mn	12734(2)	3962(4)	37410(2)	1.20(1)	1.64(2)	1.11(1)	0.075(9)	−0.09(1)	0.32(1)
O(2)	−681(1)	−1826(3)	3427(1)	2.38(8)	3.39(9)	4.4(1)	−0.87(7)	0.08(8)	2.04(9)
O(5)	1931(1)	717(3)	2187(1)	1.72(6)	4.4(1)	1.91(8)	0.49(7)	0.42(6)	0.42(7)
O(6)	1944(1)	3574(3)	4243(1)	2.79(8)	2.67(9)	4.0(1)	−0.88(7)	−0.84(8)	−0.29(8)
O(7)	−666(1)	3051(2)	2920(1)	1.25(5)	1.61(7)	1.28(6)	0.13(5)	0.07(5)	−0.19(5)
O(8)	−827(1)	4694(2)	4015(1)	1.71(6)	1.89(7)	1.84(7)	0.18(5)	0.35(5)	−0.54(6)
C(2)	−456(1)	−762(3)	3066(2)	1.42(8)	2.0(1)	2.2(1)	−0.12(8)	−0.12(8)	0.27(9)
C(5)	1630(1)	604(3)	2756(2)	1.24(8)	2.4(1)	1.57(9)	0.27(7)	−0.21(7)	0.18(8)
C(6)	1685(1)	2319(3)	4045(2)	1.49(8)	2.6(1)	1.9(1)	0.03(8)	−0.40(8)	0.36(9)
C(7)	498(1)	1866(3)	3703(1)	1.23(7)	1.63(9)	0.97(8)	−0.27(7)	−0.06(6)	0.18(7)
C(8)	204(1)	3092(3)	4104(1)	1.70(8)	1.77(9)	1.03(9)	−0.23(7)	−0.12(7)	−0.19(8)
C(9)	−451(1)	3610(3)	3643(1)	1.56(8)	1.30(9)	1.42(9)	−0.17(7)	0.46(7)	−0.10(7)
C(10)	−1503(1)	5078(4)	3533(2)	1.36(9)	2.3(1)	3.9(1)	0.22(8)	0.40(9)	−1.1(1)
C(11)	1723(1)	−2066(3)	3897(2)	2.27(9)	1.8(1)	2.4(1)	0.53(8)	−0.09(9)	0.53(9)
C(12)	1002(1)	−2211(3)	3904(2)	2.28(9)	1.8(1)	2.8(1)	−0.1(8)	−0.29(9)	0.96(9)
C(13)	841(1)	−1248(4)	4598(2)	2.4(1)	3.2(1)	2.8(1)	0.36(9)	0.81(9)	1.9(1)
C(14)	1460(2)	−523(4)	5017(2)	3.5(1)	2.9(1)	1.2(1)	0.66(9)	−0.06(9)	1.02(9)
C(15)	2006(1)	−1029(3)	4576(2)	2.19(9)	2.2(1)	2.0(1)	0.41(9)	−0.64(9)	0.76(9)

bond increases in the series $Cr(CO)_6 < Mo(CO)_6 < W(CO)_6$, elimination of the CO group becomes more difficult [24,26]. Therefore we may suppose that under the conditions employed (60°C, THF), VIb, unlike VIa, undergoes further CO loss at molybdenum, thus opening up a site for coordination of another molecule of I (Scheme 1).

Chromium has a much smaller covalent radius than Mo and W (1.23 vs. 1.39 and 1.40 Å [10]). Therefore, in a hypothetical complex VI with M = Cr, the Mn–M, M–C(7) and M–O(7) bonds should be correspondingly shorter and hence the C(7)C(8)C(9) and C(8)C(9)O(7) angles should be smaller than those in VIa (where these angles are even smaller than those in IX). Thus, the formation of a 5-membered metallacycle with M = Cr is sterically less favourable than that of a 5-membered metallacycle with M = Mo or W. This is probably the reason why I does not react with $Cr(CO)_5(THF)$ under the conditions employed.

It is noteworthy that under the same conditions the allenylidene complex $Cp(OC)_2Mn{=}C{=}C{=}CPh_2$ (X) does not react with carbonyl derivatives of Group VI metals.

Experimental

All operations were performed in nitrogen atmosphere, using absolute solvents saturated with nitrogen. Complexes I, II and X were prepared as reported elsewhere [27]. Photochemical reactions were performed using a PRK-7 mercury-quartz lamp (1000 W) and a quartz Schlenk vessel fitted with a water jacket. For column chromatography, Chemapol (Czechoslovakia) 100 × 160 μ silica gel was used. IR spectra were recorded with an UR-20 Zeiss spectrometer, ^1H NMR spectra with an Perkin–Elmer R20 (60 MHz) spectrometer, and ^{13}C NMR spectra with a Bruker HX-90 (22.63 MHz) spectrometer. Mass spectra were measured using an MS-30 spectrometer (ionizing electron energy 70 eV, temperature of ion source 200°C, temperature of injection system 20°C).

X-Ray experiments were carried out with a Syntex $P2_1$ four-circle autodiffractometer (graphite monochromated Mo-K_α radiation) at −120°C. Calculations were performed with an Eclipse S/200 computer using INEXTL programs [28]. The crystal data and experimental details are listed in Table 5. For VIa reflection intensities were corrected for absorption taking into account a real crystal shape (an irregular parallelepiped of size 0.03 × 0.06 × 0.015 mm) according to ref. 29. Both structures were solved by convenient Patterson and Fourier methods and refined by full matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal factors. In VIa the hydrogen atoms (methyl ones were located from the difference synthesis, others placed in calculated positions) were included as fixed contributions with $B_{iso} = 3.5$ Å^2. In VII all the hydrogens were located from the difference synthesis and refined isotropically. The positional and thermal atomic parameters are listed in Tables 6 and 7.

Reaction of I with $W(CO)_5(THF)$

0.4 g (1.54 mmol) of I was added to a solution of $W(CO)_5(THF)$ prepared by UV irradiation of 1.8 g (5.11 mmol) of $W(CO)_6$ in 180 ml of THF for 2 h at 4°C. The mixture was refluxed until complete disappearance of I (controlled by thin-layer chromatography), the yellow colour of the mixture turning to dark brown. The

TABLE 7

COORDINATES ($\times 10^3$) AND B_{iso} (Å^2) OF THE HYDROGEN ATOMS

Atom	Structure VIa			Structure VII			
	x	y	z	x	y	z	B_{iso}
H[C(8)]	595	114	182	39(1)	357(3)	456(2)	2.2(6)
H[C(10)]	584	−110	203	−175(1)	403(4)	349(2)	2.1(6)
H′[C(10)]	470	−98	65	−144(1)	555(4)	293(2)	4.2(8)
H″[C(10)]	680	−118	84	−169(1)	577(4)	387(2)	2.3(6)
H[C(11)]	86	281	469	250(1)	−76(4)	471(2)	3.7(7)
H[C(12)]	229	167	551	154(2)	21(4)	554(2)	4.9(8)
H[C(13)]	537	156	467	42(1)	−118(4)	477(2)	3.3(7)
H[C(14)]	580	262	336	66(1)	−296(4)	353(2)	2.9(7)
H[C(15)]	225	337	334	191(1)	−262(4)	353(2)	3.1(7)

solvent was removed in vacuo, and the residue was chromatographed on SiO_2. A dark-brown zone was eluted by a petroleum ether/ether mixture (9/1), giving 0.21 g (24%) of VIa isolated as dark-brown crystals, m.p. 116–120°C (dec.). Found: C, 32.97; H, 1.83; Mn, 10.35. $C_{15}H_9MnO_8W$ calcd.: C, 32.40; H, 1.63; Mn, 9.88%. Mass spectrum (m/z, for ^{184}W): 556 $[M]^+$; 528 $[M-CO]^+$; 500 $[M-2CO]^+$; 472 $[M-3CO]^+$; 444 $[M-4CO]^+$; 416 $[M-5CO]^+$; 388 $[M-6CO]^+$; 120 $[CpMn]^+$.

Reaction of V with W(CO)$_5$(THF)

$W(CO)_5(THF)$ solution was prepared by UV irradiation (2 h, 4°C) of 2.70 g (7.67 mmol) of $W(CO)_6$ in 150 ml of THF. The reaction of this solution with 2.0 g (7.68 mmol) of V was performed as above, yielding 0.93 g (21.8%) of VIa, characterized by m.p. and IR spectrum.

Reaction of I with Mo(CO)$_5$(THF)

0.5 g (1.22 mmol) of I was added to a solution of $Mo(CO)_5(THF)$ prepared from 1.0 g (3.83 mmol) of $Mo(CO)_6$ in 40 mol of THF (UV irradiation for 1.5 h at 4°C). The mixture was stirred for 1 h at 40–60°C, then the solvent was removed in vacuo and the residue was chromatographed on SiO_2. A brown zone eluted by benzene was chromatographed once more on SiO_2. Yellow-brown and dark-brown zones were eluted by a petroleum ether/ether mixture (9/1). From the yellow-brown zone, 0.06 g (7.0%) of VIb was isolated as dark-brown crystals, m.p. 89–90°C(dec.). Found: C, 38.72; H, 2.07; Mn, 11.93. $C_{15}H_9MnMoO_8$ calcd.: C, 38.49; H, 1.94; Mn, 11.74%. Mass spectrum (m/z, for ^{98}Mo): 470$[M]^+$; 416 $[M-2CO]^+$; 360 $[M-4CO]^+$; 204 $[Cp(OC)_2Mn]^+$; 148 $[Cp(OC)Mn]^+$; 120 $[CpMn]^+$; 55 $[Mn]^+$. The dark-brown zone yielded 0.17 g (27.7%) of dark-brown crystalline VII, decomposing at 300°C without melting. Found: C, 42.86; H, 2.68; Mn, 15.52. $C_{24}H_{18}Mn_2MoO_{10}$ calcd.: C, 42.88; H, 2.70; Mn, 16.35%.

Reaction of V with Mo(CO)$_5$(THF)

0.1 g (3.84 mmol) of V was added to the $Mo(CO)_5(THF)$ solution prepared from 2.0 g (7.58 mmol) of $Mo(CO)_6$ in 150 ml of THF (2 h, 4°C). The mixture was refluxed for 1 h. Then the solvent was removed in vacuo and the residue was chromatographed on SiO_2. From a dark-brown zone, eluted by benzene, 0.26 g (20.2%) of VII was isolated and characterized by its IR spectrum.

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