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REACTIONS OF MANGANESE π-ACETYLENIC, η-VINYLIDENIC, AND η-ALLENYLIDENIC COMPLEXES WITH $Fe_2(CO)_9$. CRYSTAL AND MOLECULAR STRUCTURE OF $Cp(CO)_2Mn(\mu^2\text{-}C{=}CHCOOCH_3)Fe(CO)_4$

N.E. KOLOBOVA *, L.L. IVANOV, O.S. ZHVANKO, G.G. ALEKSANDROV
and Yu.T. STRUCHKOV
Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow (USSR)
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Summary

The interaction between $Cp(CO)_2Mn(C{=}CHCOOMe)$ (I), $Cp(CO)_2Mn(\pi\text{-}HC{\equiv}CCOOMe)$ (II), $Cp(CO)_2Mn(C{=}C{=}CPh_2)$ (III), and $Fe_2(CO)_9$ in hexane gives rise to the complexes $Cp(CO)_2Mn(\mu^2\text{-}C{=}CHCOOMe)Fe(CO)_4$ (IVa,b) and $Cp(CO)_2Mn(\mu^2\text{-}C{=}C{=}CPh_2)Fe(CO)_4$ (VIII). The structure of IVb was determined by X-ray analysis. This compound is a binuclear complex with the $Fe(CO)_4$ and $Cp(CO)_2Mn$ fragments linked by a Fe—Mn bond and a carbomethoxyvinylidenic ligand. Compound IVa is a geometrical isomer of IVb.

Introduction

The chemistry of complexes of transition metals with unsaturated carbenes is attracting more and more attention of researchers. Until now there have been obtained a number of compounds with vinylidenic and allenylidenic ligands [1—16]; however, their properties have not been studied thoroughly.

Among the reactions described there is only one example of an interaction between a vinylidenic complex, $Cp(CO)_2Mn(C{=}CHPh)$, and $Fe_2(CO)_9$, giving a binuclear compound with a hetero-atomic analogue of trimethylenemethane [17].

The present article deals with the results of studies of the reactions of manganese η-vinylidenic and π-acetylenic complexes, $Cp(CO)_2Mn(C{=}CHR)$ (I) and $Cp(CO)_2Mn(\pi\text{-}HC{=}CR)$ (II), containing an electron-withdrawing substituent (R = COOMe) in the ligand and of a η-diphenylallenylidenic complex, $Cp(CO)_2Mn(C{=}C{=}CPh_2)$ (III), with $Fe_2(CO)_9$.

Results and discussion

The reaction of (π-cyclopentadienyl)(carbomethoxyvinylidene)(dicarbonyl)-manganese (I) with diiron nonacarbonyl at 40°C in hexane results in the for-

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mation of two air-stable isomeric binuclear compounds, IVa and IVb, in a 1 : 9 ratio; the compounds were separated chromatographically with yields of 8.7 and 73.3%, respectively.

$$\underset{\text{(I)}}{\mathrm{Cp(CO)_2Mn(C{=}CHCOOMe)}} + \mathrm{Fe_2(CO)_9} \xrightarrow[\text{n-hexane}]{40^\circ\text{C; 45 min}} \underset{\text{(IVa,b)}}{\mathrm{Cp(CO)_2Mn(\mu^2\text{-}C{=}CHCOOMe)Fe(CO)_4}} \qquad (1)$$

Compound IVa was obtained in the form of red crystals with m.pt. 100—102 °C, soluble in most organic solvents; IVb is a dark-red crystalline compound with m.pt. 110—111 °C (decomposes), slightly soluble in aliphatic hydrocarbons, moderately so in ether, and readily soluble in CH_2Cl_2 and $CHCl_3$.

The interaction between the π-complex II and $Fe_2(CO)_9$ under similar conditions also furnishes compounds IVa (1.2%) and IVb (7.3%) together with other products whose composition is now under study.

$$\underset{\text{(II)}}{\mathrm{Cp(CO)_2Mn(\pi\text{-}HC{\equiv}CCOOMe)}} + \mathrm{Fe_2(CO)_9} \rightarrow \underset{\text{(IVa,b)}}{\mathrm{Cp(CO)_2Mn(\mu^2\text{-}C{=}CHCOOMe)Fe(CO)_4}} + \text{other products} \qquad (2)$$

The acetylenic π-complex II, in the course of the reaction with $Fe_2(CO)_9$, seems to undergo a partial isomerisation into the η-vinylidenic one (I).

IR spectra of IVa and IVb in cyclohexane (Table 1) show similar values of the characteristic frequencies of the double C=C bond and the carbonyl bond of COOMe, but in the absorption region of terminal carbonyls (1900—2100 cm^{-1}) the spectrum of IVa contains one band more than that of IVb; this may be related to the difference in the location of substituents at the double bond.

Mass spectra of IVa and IVb contain peaks of molecular ions with m/e 428 and also peaks of $[M - n(CO)]^+$ ions (n = 1—6) formed as a result of a successive elimination of six CO groups.

TABLE 1

IR SPECTRA (IN CYCLOHEXANE) OF COMPOUNDS IVa, IVb AND VIII (cm^{-1})

Compound:	$\nu(C{\equiv}O)$	$\nu(C{=}O)$	$\nu(C{=}C)$	$\nu(C{=}C{=}C)$
IVa	2085s, 2030s, 2010vs, 2000s, 1985s, 1925m	1702m	1545m	—
IVb	2090s, 2040m, 2015vs, 1975s, 1930m	1705m	1555m	—
VIII	2090s, 2040s, 2013vs, 1970s, 1925s	—	—	1890w

The structure of the IVb isomer was established by X-ray analysis. Crystals of IVb are monoclinic; at 20°C $a = 13.035(2)$, $b = 8.116(1)$, $c = 15.432(2)$ Å, $\beta = 97.17(1)°$, $d_{calc} = 1.75$ g/cm^3, $Z = 4$, space group $P2_1/c$. The coordinates of the atoms and their temperature factors are given in Table 2, bond lengths and valence angles can be found in Tables 3 and 4, respectively. The molecule IVb (Fig. 1) is a binuclear complex with $Fe(CO)_4$ and $Cp(CO)_2Mn$ fragments linked by the Fe—Mn bond and a bridging carbomethoxyvinylidenic ligand.

Because of the constricting effect of the ligand, the Fe—Mn distance (2.703(4) Å) is slightly smaller than the length of a usual single Fe—Mn bond in $(CO)_5MnFe(CO)_4Mn(CO)_5$ (2.80 and 2.83 Å) [18] and $Cp(CO)_2FeMn(CO)_5$ (2.84 Å) [19] having no bridging ligands and that of a Fe—Mn bond (2.760 Å) in $Cp(CO)_2Mn[C(CO)CHPh]Fe(CO)_3$ [17]. The C(7) atom of the bridging carbomethoxyvinylidenic ligand is symmetrically bonded to Fe and Mn atoms. The Fe—C(7) and Mn—C(7) bond lengths are 1.94(2) and 1.95(2) Å, respectively, and are very close to the previously found M—C (μ-vinylidene) bond length values: Fe—C 1.96(2) and 1.97(2) Å in $[Fe(CO)_4]_2(C{=}CPh_2)$ (V) [1], Mn—C 1.94(1) and 1.99(1) Å in $Cp(CO)_2Mn_2(C{=}CHPh)$ (VI) [2], Mn—C

TABLE 2

COORDINATES OF ATOMS ($\times 10^3$; Fe AND Mn $\times 10^4$) AND THEIR TEMPERATURE FACTORS

Atom	X	Y	Z	B_{iso} (Å)
Fe	6877(2)	722(3)	2444(2)	—
Mn	8433(2)	1975(4)	3574(2)	—
O(1)	843(1)	—46(2)	134(1)	5.6(3)
O(2)	634(1)	—259(2)	301(1)	6.2(3)
O(3)	537(1)	84(2)	89(1)	6.1(3)
O(4)	549(1)	256(2)	345(1)	5.7(3)
O(5)	862(1)	—158(2)	384(1)	6.5(3)
O(6)	1011(1)	196(2)	247(1)	7.4(3)
O(7)	601(1)	414(2)	118(1)	6.2(3)
O(8)	714(1)	609(2)	97(1)	5.7(3)
C(1)	784(1)	—9(2)	177(1)	4.2(4)
C(2)	656(1)	—132(2)	280(1)	4.4(4)
C(3)	595(1)	86(2)	147(1)	4.1(4)
C(4)	602(1)	185(3)	307(1)	5.3(4)
C(5)	848(1)	—17(3)	367(1)	4.9(4)
C(6)	949(2)	194(3)	292(2)	7.5(5)
C(7)	763(1)	278(2)	251(1)	3.5(3)
C(8)	762(1)	418(2)	209(1)	4.1(4)
C(9)	686(2)	472(3)	134(1)	5.4(4)
C(10)	645(1)	670(3)	21(1)	5.9(5)
C(11)	939(1)	302(2)	466(1)	4.7(4)
C(12)	867(2)	204(3)	496(1)	6.5(5)
C(13)	769(1)	262(2)	471(1)	5.2(4)
C(14)	780(1)	405(2)	420(1)	5.1(4)
C(15)	886(1)	429(2)	417(1)	5.2(4)

ANISOTROPIC TEMPERATURE FACTORS OF Fe AND Mn ATOMS EXPRESSED AS: $T = \exp(-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*))$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	3.2(1)	4.1(1)	3.2(1)	—0.1(1)	0.27(9)	—0.1(1)
Mn	3.1(1)	4.3(1)	3.5(1)	0.0(1)	0.13(9)	0.0(1)

TABLE 3

BOND LENGTHS d(Å)

Bond	d	Bond	d	Bond	d
Fe—Mn	2.703(4)	Mn—C(12)	2.13(2)	O(7)—C(9)	1.21(2)
Fe—C(1)	1.85(2)	Mn—C(13)	2.18(2)	O(8)—C(9)	1.32(2)
Fe—C(2)	1.82(2)	Mn—C(14)	2.16(2)	O(8)—C(10)	1.46(2)
Fe—C(3)	1.82(2)	Mn—C(15)	2.13(2)	C(7)—C(8)	1.30(2)
Fe—C(4)	1.82(2)	O(1)—C(1)	1.12(2)	C(8)—C(9)	1.49(3)
Fe—C(7)	1.94(2)	O(2)—C(2)	1.13(2)	C(11)—C(12)	1.36(3)
Mn—C(5)	1.75(2)	O(3)—C(3)	1.09(2)	C(11)—C(15)	1.41(3)
Mn—C(6)	1.80(2)	O(4)—C(4)	1.12(2)	C(12)—C(13)	1.37(3)
Mn—C(7)	1.95(2)	O(5)—C(5)	1.18(3)	C(13)—C(14)	1.42(3)
Mn—C(11)	2.14(2)	O(6)—C(6)	1.14(3)	C(14)—C(15)	1.40(3)

1.979(7) and 1.971(7) Å in $[CpMn(CO)_2]_2(C{=}CH_2)$ (VII) [12].

The metal—vinylidenic fragment FeMnC(7)C(8) is planar with the length of the double C=C bond 1.30 Å being close to the standard value (1.337 Å) [20], and which is comparable with the values found for other μ-vinylidenic complexes (VI and VII) (1.30—1.35 Å). As the ethylenic bond is surrounded by four different substituents and an asymmetric centre (Mn atom), the molecules of IVa and IVb can each exist in the form of two geometrical isomers, A (*Z* isomer) and B (*E* isomer), each of them having a corresponding enantiomer (A′, B′) (Fig. 2). The centrosymmetric nature of the $P2_1/c$ space group points to the presence of both enantiomers, B and B′, in IVb. Likewise, IVa is a racemic mixture of A and A′ enantiomers.

The vinylidenic ligand is twisted around the double C=C bond by 7° (in VI

TABLE 4

VALENCE ANGLES ω (degrees)

Angle	ω	Angle	ω
MnFeC(1)	89.5(6)	C(5)MnC(7)	114.6(8)
MnFeC(2)	109.2(6)	C(6)MnC(7)	84.1(9)
MnFeC(3)	152.2(6)	C(9)O(8)C(10)	117(1)
MnFeC(4)	86.0(6)	FeC(1)O(1)	175(2)
MnFeC(7)	46.1(5)	FeC(2)O(2)	178(2)
FeMnC(5)	72.2(7)	FeC(3)O(3)	176(2)
FeMnC(6)	101.3(7)	FeC(4)O(4)	179(2)
FeMnC(7)	45.8(5)	MnC(5)O(5)	170(2)
C(1)FeC(2)	92.6(8)	MnC(6)O(6)	176(2)
C(1)FeC(3)	89.9(8)	FeC(7)Mn	88.1(7)
C(1)FeC(4)	170.6(9)	FeC(7)C(8)	139(1)
C(1)FeC(7)	87.6(7)	MnC(7)C(8)	133(1)
C(2)FeC(3)	98.6(8)	C(7)C(8)C(9)	127(2)
C(2)FeC(4)	96.7(9)	O(7)C(9)O(8)	122(2)
C(2)FeC(7)	155.3(8)	O(7)C(9)C(8)	124(2)
C(3)FeC(4)	90.3(8)	O(8)C(9)C(8)	113(2)
C(3)FeC(7)	106.2(7)	C(12)C(11)C(15)	107(2)
C(4)FeC(7)	83.3(8)	C(11)C(12)C(13)	111(2)
C(5)MnC(6)	90.8(9)	C(12)C(13)C(14)	106(2)
		C(13)C(14)C(15)	108(2)
		C(11)C(15)C(14)	108(2)

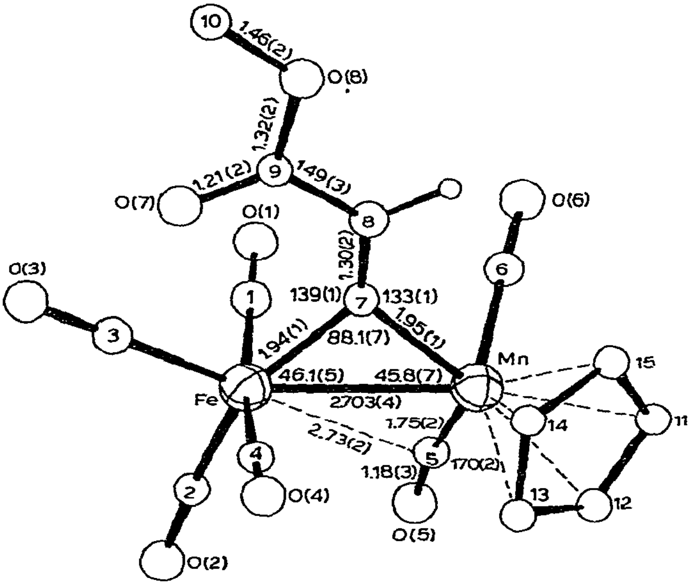
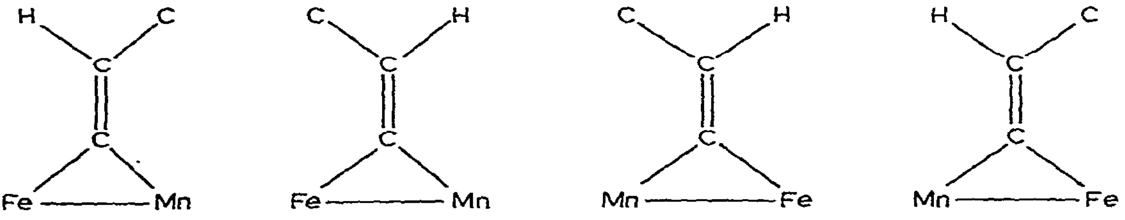


Fig. 1. The structure of $Cp(CO)_2Mn(\mu^2\text{-}C{=}CHCOOMe)Fe(CO)_4$. The location of the H atom bonded to the C(8) atom of the vinylidenic ligand is also shown on the basis of geometrical calculations.

and VII this angle is 7 and 11°, respectively), that is, the dimetal-carboxyvinylidenic system is non-planar with the deviation of the C(9) and O(7), O(8) and C(10) atoms from the FeMnC(7)C(8) plane being −0.18, −0.65, 0.03, and −0.08 Å, respectively.

As in the binuclear complexes VI and VII with a bridging vinylidenic ligand, the orientation of the CO groups at the Mn atom is different: the FeMnC(5) angle (72.2(7)°) is much smaller than the FeMnC(6) angle (101.3(7)°). Thus, the C(5)—O(5) carbonyl is of a "semi-bridging" kind due to a weak interaction of its C(5) atom with the second metal atom (Fe···C(5) 2.73(2) Å). This interaction leads to a stronger perturbation of the linearity of the unsymmetrical MnC(5)O(5) bridge fragment (170(2)°) as against the MnC(6)O(6) fragment (176(2)°) with a purely terminal CO ligand. A similar perturbation in MCO fragments of unsymmetrical bridging CO groups was found for VI, VII, and a number of other carbonyl complexes [21].



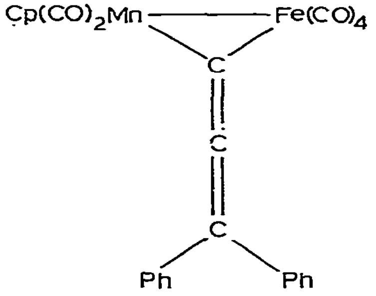
(A) (B) (A') (B')

Fig. 2. Structures of the isomers of IVa and IVb.

The interaction between the diphenylallenylidenic complex III and $Fe_2(CO)_9$ under the same conditions gives rise to complex VIII, the sole metal carbonyl product, with a 65% yield, according to eq. 3:

$$\underset{\text{(III)}}{Cp(CO)_2Mn(C{=}C{=}CPh_2)} + Fe_2(CO)_9 \rightarrow \underset{\text{(VIII)}}{Cp(CO)_2(\mu^2\text{-}C{=}C{=}CPh_2)Fe(CO)_4} \qquad (3)$$

Complex VIII is a violet crystalline product, stable in air, m.pt. 99—101° (decomposes). The product is readily soluble in all organic solvents. The IR spectrum of VIII in cyclohexane (Table 1) contains 5 absorption bands of terminal CO groups and one band (1890 cm^{-1}) which we attribute to the vibrations of the allenylidenic chain of the ligand, $C{=}C{=}CPh_2$, on the basis of an earlier study [15]. In the mass spectrum of VIII there were found ions with *m/e* 450 and 394 corresponding to $M^+ - 3\,CO$ and $M^+ - 5\,CO$ and also an ion with the mass of the $Cp(CO)_2Mn(C_3Ph_2)$ fragment. A comparison of these results with the data of elemental analysis and a comparison between ^{13}C NMR spectra (Table 5) of the obtained complex VIII and the binuclear complex $Cp(CO)_2Mn_2(\mu^2\text{-}C{=}C{=}CPh_2)$ (IX), whose structure is known [15], made it possible to propose for VIII a structure analogous to that of IX:



(VIII)

TABLE 5

^{13}C NMR CHEMICAL SHIFTS, δ, IN COMPOUNDS VIII—IX (ppm)

Compound	Cp	CO	$C(1){=}C(2){=}C(3)Ph_2$		
			C(1)	C(2)	C(3)
VIII	88.64	207.46	333.25	106.61	201.12
IX	88.00	231.82 235.70	339.33	105.93	204.11

Compound	C_6H_5			
	C_{c1}	C_{ortho}	C_{meta}	C_{para}
VIII	140.39	128.36	128.89	126.48
IX	140.98	128.87	128.66	126.31

Experimental

Absolute solvents saturated with nitrogen were used in the experiments. All operations were conducted in an atmosphere of nitrogen. IR spectra were taken on a UR-20 (Zeiss) spectrometer. Mass spectra were taken on a AEI-MS-30 mass spectrometer with a DS-50 data processing unit; ionisation voltage was 70 eV, the temperature of the ionisation chamber 200—225°C, the temperature of the leak-in system 100—150°C. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer (20 MHz). X-ray structure experiments were conducted on a Hilger-Watts diffractometer, λCu-K_α, $\theta/2\theta$ scanning, 1100 reflections with $F^2 \geqslant 3\sigma$, heavy atom method, least-square refinement in a complete-matrix anisotropic(Fe, Mn)-isotropic approach, $R = 0.078$, $R_W = 0.088$.

Reaction of Cp(CO)$_2$Mn(C=CHCOOCH$_3$) (I) with Fe$_2$(CO)$_9$

2.0 g (0.0055 mol) of $Fe_2(CO)_9$ were added to a solution of 1.05 g (0.0040 mol) of I in 150 ml of hexane. A dark-red compound precipitated after stirring (45 min at 40°C). The solution was decanted from the precipitate, the precipitate washed with hexane (3 × 5 ml) and dissolved in ether. The unreacted $Fe_2(CO)_9$ was filtered off (0.56 g) and the filtrate reduced in volume. 1.26 g of IVb were isolated (73.3%). Analysis. Found: C, 42.07; H, 2.41; Fe, 12.73; Mn, 12.65. $C_{15}H_9FeMnO_8$ calcd.: C, 42.09; H, 2.12; Fe, 13.05; Mn, 12.84%. Mass spectrum (*m/e*): 428 $[M]^+$; 400 $[M - CO]^+$; 372 $[M - 2\,CO]^+$; 344 $[M - 3\,CO]^+$; 316 $[M - 4\,CO]^+$; 288 $[M - 5\,CO]^+$; 260 $[M - 6\,CO]^+$; 204 $[CpMn(CO)_3]^+$; 186 $[Cp_2Fe]^+$; 176 $[CpMn(CO)_2]^+$; 120 $[CpMn]^+$.

The decanted solution was evaporated to dryness and the product separated chromatographically on SiO_2 (4°C, petroleum ether/ether, 9/1, as eluent). The following zones were eluted: dark-green (0.05 g of $Fe_3(CO)_{12}$), dark-red (0.15 g (8.7%) of IVa). Analysis. Found: C, 42.30; H, 2.51; Fe, 13.04; Mn, 12.66. $C_{15}H_9FeMnO_8$ calcd.: C, 42.09; H, 2.12; Fe, 13.05; Mn, 12.84%, Mass spectrum (*m/e*): 372 $[M - 2\,CO]^+$; 344 $[M - 3\,CO]^+$; 316 $[M - 4\,CO]^+$; 288 $[M - 5\,CO]^+$; 260 $[M - 6\,CO]^+$; 204 $[CpMn(CO)_3]^+$; 186 $[Cp_2Fe]^+$; 176 $[CpMn(CO)_2]^+$; 148 $[CpMn(CO)]^+$; 120 $[CpMn]^+$.

Reaction of Cp(CO)$_2$Mn(CO)$_2$Mn(C=C=CPh$_2$) (III) with Fe$_2$(CO)$_9$

1.0 g (0.0027 mol) of $Fe_2(CO)_9$ was added to a solution of 0.67 g (0.018 mol) of III in 150 ml of hexane. After 45 min of stirring at 40°C the unreacted $Fe_2(CO)_9$ (0.47 g) was filtered off and the solvent removed from the solution in vacuum. 0.63 g of VIII (64.2%) were obtained by extraction with a hexane/ether (4/1) mixture. Analysis. Found: C, 58.62; H, 2.74; Fe, 10.41; Mn, 9.80. $C_{24}H_{15}FeMnO_4$ calcd.: C, 58.45; H, 2.83; Fe, 10.46; Mn, 10.28%. Mass spectrum (*m/e*): 450 $[M - 3\,CO]^+$; 394 $[M - 5\,CO]^+$; 366 $[Cp(CO)_2Mn(C{=}C{=}CPh_2)]^+$; 204 $[CpMn(CO)_3]^+$; 186 $[Cp_2Fe]^+$; 176 $[CpFeMn]^+$; 120$[CpMn]^+$.

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