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CHEMISTRY OF VINYLIDENE COMPLEXES

IV *. SYNTHESIS AND THE CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta^5\text{-}C_5H_5)MnOs_3(\mu_2\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$, AN UNUSUAL HETEROMETALLIC CLUSTER

A.B. ANTONOVA*, S.V. KOVALENKO, E.D. KORNIYETS, A.A. JOHANSSON,

Institute of Chemistry and Chemical Technology, Siberian Branch of the Academy of Sciences of the U.S.S.R., K. Marx Str. 42, Krasnoyarsk, 660049 (U.S.S.R.)

Yu.T. STRUCHKOV* and A.I. YANOVSKY

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov Str. 28, Moscow, 117813 (U.S.S.R.)

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Summary

By the reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with $H_2Os_3(CO)_{10}$ (II) the tetranuclear mixed-metal complex $CpMnOs_3(\mu_2\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (III) was prepared. An X-ray study of the structure of III showed that it is a spiked, tetranuclear cluster with the Mn atom linked to one of the vertices of the osmium triangle; the Mn–Os bond is bridged by CO and CH=CHPh groups, the latter being σ-bonded to Os and η^2-coordinated by Mn. In the course of the formation of III, hydrogenation and *n*-π rearrangement of the initial phenylvinylidene ligand take place. In solution, complex III readily eliminates the $[CpMn(CO)_2]$ fragment to give triosmium clusters containing unsaturated organic ligands: $HOs_3(\mu_2\text{-}CH{=}CHPh)(CO)_{10}$, $H_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$, and $H_2Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$.

Introduction

Mononuclear vinylidene complexes of transition metals react smoothly with unsaturated metal-containing moieties and molecules to afford the addition products [1,2]. These reactions not only represent a good method of synthesising various polynuclear heterometallic compounds, but also provide new opportunities for the

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[*] For part III see ref. 1.

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discovery and investigation of transformations of unsaturated organic ligands occurring in the coordination sphere of several transition metal atoms.

It is known that reactions of the vinylidene complexes $Cp(CO)_2Mn{=}C{=}CHR$ (R = Ph or COOMe) with coordinatively unsaturated units $[ML_n]$ (ML_n = $CpMn(CO)_2$ [3,4], $CpRe(CO)_2$ [5], $Fe(CO)_4$ [6,7], $W(CO)_5$ [8], $Pt(PR_3)_2$ [1,9]) lead to binuclear compounds with Mn–M bonds. As a rule, in these reactions the C=CHR group is retained and only transforms to a bridging form.

We have shown [6] the possibility of transformation of a vinylidene ligand at the bimetallic centre of two different metals by the reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with $Fe_2(CO)_9$, which affords the binuclear complex, $Cp(CO)_2Mn[C(CO)CHPh]Fe(CO)_3$, containing the organic ligand with a carbonylated α-carbon atom.

Previously [2] we have reported the reaction of vinylidene complex I with the unsaturated carbonyl-hydride cluster $H_2Os_3(CO)_{10}$(II), which leads to the formation of a $MnOs_3$ cluster and transformation (hydrogenation and isomerisation) of the phenylvinylidene group in this heteronuclear system. The results of an X-ray study of the product of this reaction, $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (III), are reported in the present paper. Complex III is the first example of a $MnOs_3$ cluster compound for which an X-ray analysis has been performed.

Results and discussion

The dark-red crystalline cluster $CpMnOs_3(CH{=}CHPh)(H)(CO)_{12}$ (III) is a major product of the reaction between $Cp(CO)_2Mn{=}C{=}CHPh$ (I) and $H_2Os_3(CO)_{10}$ (II). It is readily soluble in organic solvents and moderately stable in solutions in tetrahydrofuran or 1,4-dioxane. However, in non-polar solvents complex III rapidly decomposes forming the triosmium clusters $HOs_3(\mu_2\text{-}CH{=}CHPh)(CO)_{10}$, $H_2Os_3(\mu_3\text{-}CH{\equiv}CPh)(CO)_9$, and $H_2Os_3(\mu_3\text{-}C{=}CHPh)(CO)_9$ [2].

The IR spectrum of III (in cyclohexane) shows terminal carbonyl stretching bands at 2127m, 2072s, 2053sh, 2047vs, 2030s, 1997vs, 1980m, 1950sh and 1933m cm^{-1} and the band of a bridging CO group at 1790 cm^{-1}. The ^1H NMR spectrum (in $CDCl_3$) shows a singlet resonance of one hydride atom at δ −22.2 ppm, two doublets of olefinic hydrogens of the *trans*-CH=CHPh group at δ 3.75 and 9.34 ppm (J 14.2 Hz), and proton signals of the η^5-cyclopentadienyl and phenyl rings. In the mass spectrum of III the parent ion peak is absent; the peak with largest m/z, 958, corresponds to the ion $[HOs_3(C_2H_2Ph)(CO)_{10}]^+$. Besides the peaks of the fragmentation products of this ion, the mass spectrum exhibits intense peaks of $[CpMn(CO)_3]^+$ and its fragments.

On the basis of spectral and elemental analysis data, complex III was formulated as $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$. In order to establish the structure of III unequivocally, an X-ray diffraction study was carried out. A single crystal was grown from a solution of III in 1,4-dioxane at −15°C. Complex III crystallizes as a solvate with 1.5 molecules of dioxane.

The molecular structure of III is shown in Fig. 1; bond lengths and angles are given in Tables 1 and 2, respectively.

The metal framework of III consists of an osmium triangle with the Mn atom linked to the Os(1) atom. Two Os–Os edges, Os(1)–Os(2) 2.851(2) Å and Os(2)–Os(3) 2.889(1) Å, are almost equal and are close to the values found for a single Os–Os bond, e.g., 2.877 Å in $Os_3(CO)_{12}$ [10]. The Os(1)–Os(3) distance of 3.069(1) Å is substantially longer and corresponds to the length of the Os–Os bond bridged by one hydride atom: e.g., 2.989 Å in $HOs_3(\mu\text{-}H)(CO)_{11}$ [10], 3.019 Å in $HOs_3(\mu\text{-}H)(CO)_{10}(PPh_3)$ [11], 3.070 Å in $(\mu\text{-}H)_2Os_3Re_2(CO)_{20}$ [12]. The position of a μ-hydride atom in III as a bridge of the Os(1)–Os(3) edge can also be inferred from a comparison of the angles defined by the equatorial CO groups and the Os–Os bonds. While the Os–Os–CO angles adjoining the Os(1)–Os(2) and Os(2)–Os(3) bonds are less than 100°, those at the Os(1)–Os(3) bond are much greater: the Os(1)Os(3)C(8) and Os(3)Os(1)C(12) angles are 119.2(7)° and 108.0(7)°, respectively.

Each of the Os(2) and Os(3) atoms bears four CO groups in the usual conforma-

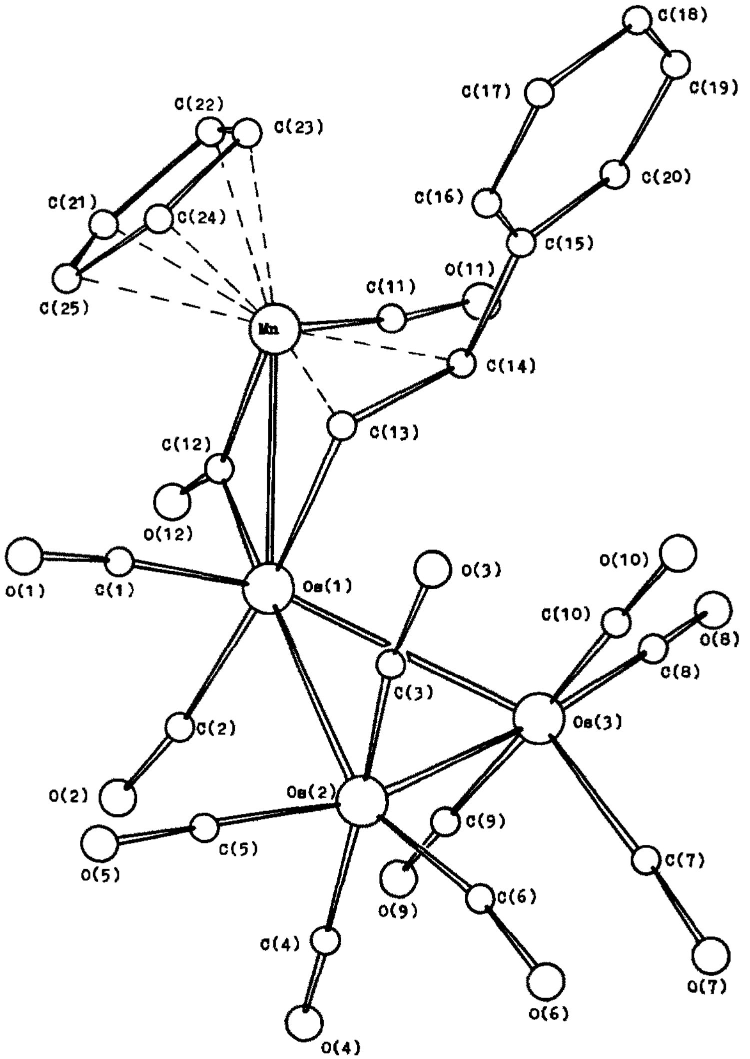

Fig. 1. Molecular structure of $CpMnOs_3(\mu_2\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (III) showing the atomic numbering scheme.

TABLE 1

BOND LENGTHS IN III [a]

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
Os(1)-Os(2)	2.851(2)	Mn-C(21)	2.16(4)	C(15)-C(20)	1.33(4)
Os(1)-Os(3)	3.069(1)	Mn-C(22)	2.18(4)	C(16)-C(17)	1.48(5)
Os(2)-Os(3)	2.889(1)	Mn-C(23)	2.12(3)	C(17)-C(18)	1.44(5)
Os(1)-Mn	2.765(4)	Mn-C(24)	2.17(4)	C(18)-C(19)	1.42(5)
Os(1)-C(1)	1.88(2)	Mn-C(25)	2.23(3)	C(19)-C(20)	1.42(5)
Os(1)-C(2)	2.00(3)	C(1)-O(1)	1.11(3)	C(21)-C(22)	1.43(5)
Os(1)-C(12)	2.16(3)	C(2)-O(2)	1.09(3)	C(21)-C(25)	1.41(5)
Os(1)-C(13)	2.11(3)	C(3)-O(3)	1.32(4)	C(22)-C(23)	1.42(5)
Os(2)-C(3)	1.74(4)	C(4)-O(4)	1.12(3)	C(23)-C(24)	1.41(5)
Os(2)-C(4)	1.97(3)	C(5)-O(5)	1.15(3)	C(24)-C(25)	1.53(5)
Os(2)-C(5)	1.91(3)	C(6)-O(6)	1.24(4)	O$_D$(11)-C$_D$(11)	1.40(5)
Os(2)-C(6)	1.79(4)	C(7)-O(7)	1.19(4)	O$_D$(11)-C$_D$(12)	1.45(5)
Os(3)-C(7)	1.90(3)	C(8)-O(8)	1.12(3)	C$_D$(11)-C$_D$(12')	1.51(6)
Os(3)-C(8)	1.91(2)	C(9)-O(9)	1.08(3)	O$_D$(21)-C$_D$(21)	1.31(11)
Os(3)-C(9)	2.04(2)	C(10)-O(10)	1.23(4)	O$_D$(21)-C$_D$(24)	1.47(9)
Os(3)-C(10)	1.85(3)	C(11)-O(11)	1.21(4)	O$_D$(22)-C$_D$(22)	1.43(11)
Mn-C(11)	1.70(3)	C(12)-O(12)	1.20(3)	O$_D$(22)-C$_D$(23)	1.28(9)
Mn-C(12)	1.89(3)	C(13)-C(14)	1.46(4)	C$_D$(21)-C$_D$(22)	1.52(13)
Mn-C(13)	2.08(3)	C(14)-C(15)	1.49(4)	C$_D$(23)-C$_D$(24)	1.61(11)
Mn-C(14)	2.28(2)	C(15)-C(16)	1.44(4)		

[a] Throughout this paper, C$_D$ and O$_D$ refer to the atoms of solvating dioxane molecules.

tion. The Os(1) atom has two terminal CO groups and a bridging C(12)O(12) carbonyl, and is σ-bonded to two Os and Mn atoms and the phenylvinyl group. The coordination polyhedron of the Os(1) atom can be regarded as a distorted octahedron (see Fig. 2), if one assumes that three atoms, Mn, C(12), and C(13), occupy two coordination sites.

The Mn atom is coordinated by the η^5-cyclopentadienyl ring, terminal C(11)O(11) and bridging C(12)O(12) carbonyls, the Os(1) atom, and the C(13)=C(14) double bond of the phenylvinyl group. The Mn-Os(1) distance of 2.765(4) Å is somewhat shorter than the sum of the covalent radii, which is equal to 2.82 Å (r_{Mn} 1.38 Å [13], r_{Os} 1.44 Å [10]). This shortening is evidently due to the presence of bridging ligands. The Mn-Os(1) bond vector is inclined to the plane of the osmium triangle at an angle of 30°.

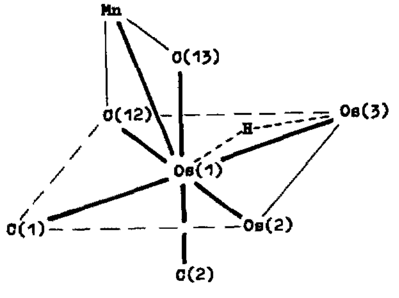

Fig. 2. Idealized scheme of the Os(1) coordination sphere.

The phenylvinyl group is in an apical position to the Os(1) atom. The length of the Os(1)–C(13) σ-bond (2.11(3) Å) is close to that found in other vinylosmium compounds, e.g., 2.107 Å in $HOs_3(\mu_2\text{-}CH{=}CH_2)(CO)_{10}$ [14], 2.15 Å in $HOs_3(\mu_2\text{-}CPh{=}CHPh)(CO)_{10}$ [15]. Due to η^2-coordination, the C(13)=C(14) double bond is elongated to 1.46(4) Å. This value is comparable, within a standard deviation, to those found in other η-olefinic manganese complexes, e.g., 1.395 Å in $Cp(CO)_2Mn[\eta^2\text{-}PhCH{=}CHP(O)(OEt)_2]$ [16], 1.39 Å in $Cp(CO)_2Mn[\eta^2\text{-}CH_2{=}CPh(OCOMe)]$ [17]; and in homonuclear μ_2-σ : η^2-vinylic compounds of manganese and osmium, e.g., 1.372 Å in $Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7$ [18], 1.396 Å in $HOs_3(\mu_2\text{-}CH{=}CH_2)(CO)_{10}$ [14], and 1.36 Å in $HOs_3(\mu_2\text{-}CPh{=}CHPh)(CO)_{10}$ [15]. Nevertheless, the torsion angle of 178(3)° for Os(1)C(13)C(14)C(15), as well as the

TABLE 2

BOND ANGLES IN III

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Os(2)Os(1)Os(3)	58.28(3)	Os(1)Os(3)Os(2)	57.09(3)	Os(3)C(7)O(7)	178(2)
Os(2)Os(1)Mn	148.5(1)	Os(1)Os(3)C(7)	141.4(8)	Os(3)C(8)O(8)	178(2)
Os(2)Os(1)C(1)	95.7(8)	Os(1)Os(3)C(8)	119.2(7)	Os(3)C(9)O(9)	177(2)
Os(2)Os(1)C(2)	87.5(8)	Os(1)Os(3)C(9)	84.9(6)	Os(3)C(10)O(10)	172(3)
Os(2)Os(1)C(12)	162.1(8)	Os(1)Os(3)C(10)	91(1)	MnC(11)O(11)	175(3)
Os(2)Os(1)C(13)	101.3(8)	Os(2)Os(3)C(7)	84.5(8)	Os(1)C(12)Mn	86(1)
Os(3)Os(1)Mn	110.07(9)	Os(2)Os(3)C(8)	175.3(7)	Os(1)C(12)O(12)	131(2)
Os(3)Os(1)C(1)	153.4(8)	Os(2)Os(3)C(9)	94.5(6)	MnC(12)O(12)	143(2)
Os(3)Os(1)C(2)	90.8(8)	Os(2)Os(3)C(10)	82(1)	Os(1)C(13)Mn	83(1)
Os(3)Os(1)C(12)	108.0(7)	C(7)Os(3)C(8)	99(1)	Os(1)C(13)C(14)	120(2)
Os(3)Os(1)C(13)	94.7(8)	C(7)Os(3)C(9)	94(1)	MnC(13)C(14)	78(1)
MnOs(1)C(1)	89.1(8)	C(7)Os(3)C(10)	88(1)	MnC(14)C(13)	63(1)
MnOs(1)C(2)	123.4(9)	C(8)Os(3)C(9)	88(1)	MnC(14)C(15)	115(2)
MnOs(1)C(12)	42.9(9)	C(8)Os(3)C(10)	95(1)	C(13)C(14)C(15)	122(2)
MnOs(1)C(13)	48.1(9)	C(9)Os(3)C(10)	176(1)	C(14)C(15)C(16)	121(2)
C(1)Os(1)C(2)	94(1)	Os(1)MnC(11)	104(1)	C(14)C(15)C(20)	118(2)
C(1)Os(1)C(12)	99(1)	Os(1)MnC(12)	51.3(8)	C(16)C(15)C(20)	120(3)
C(1)Os(1)C(13)	84(1)	Os(1)MnC(13)	49.2(7)	C(15)C(16)C(17)	120(3)
C(2)Os(1)C(12)	81(1)	Os(1)MnC(14)	75.5(6)	C(16)C(17)C(18)	116(3)
C(2)Os(1)C(13)	171(1)	Os(1)MnCp[a]	131.2	C(17)C(18)C(19)	120(3)
C(12)Os(1)C(13)	91(1)	C(11)MnC(12)	81(1)	C(18)C(19)C(20)	120(3)
Os(1)Os(2)Os(3)	64.63(4)	C(11)MnC(13)	111(1)	C(15)C(20)C(19)	123(3)
Os(1)Os(2)C(3)	76.4(9)	C(11)MnC(14)	78(1)	C(22)C(21)C(25)	112(3)
Os(1)Os(2)C(4)	95.2(8)	C(11)MnCp[a]	122	C(21)C(22)C(23)	106(3)
Os(1)Os(2)C(5)	95.2(8)	C(12)MnC(13)	100(1)	C(22)C(23)C(24)	111(3)
Os(1)Os(2)C(6)	159(1)	C(12)MnC(14)	115(1)	C(23)C(24)C(25)	107(3)
Os(3)Os(2)C(3)	94.4(9)	C(12)MnCp[a]	116	C(21)C(25)C(24)	104(3)
Os(3)Os(2)C(4)	81.2(8)	C(13)MnC(14)	38.8(9)	$C_D(11)O_D(11)C_D(12)$	116(3)
Os(3)Os(2)C(5)	158.3(8)	C(13)MnCp[a]	119	$O_D(11)C_D(11)C_D(12')$	114(3)
Os(3)Os(2)C(6)	99(1)	C(14)MnCp[a]	128	$O_D(11)C_D(12)C_D(11')$	108(3)
C(3)Os(2)C(4)	172(1)	Os(1)C(1)O(1)	172(2)	$C_D(21)O_D(21)C_D(24)$	118(6)
C(3)Os(2)C(5)	88(1)	Os(1)C(2)O(2)	174(3)	$C_D(22)O_D(22)C_D(23)$	121(6)
C(3)Os(2)C(6)	93(1)	Os(2)C(3)O(3)	168(2)	$O_D(21)C_D(21)C_D(22)$	116(8)
C(4)Os(2)C(5)	93(1)	Os(2)C(4)O(4)	176(2)	$O_D(22)C_D(22)C_D(21)$	117(7)
C(4)Os(2)C(6)	97(1)	Os(2)C(5)O(5)	176(2)	$O_D(22)C_D(23)C_D(24)$	120(6)
C(5)Os(2)C(6)	102(1)	Os(2)C(6)O(6)	170(3)	$O_D(21)C_D(24)C_D(23)$	109(6)

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[a] Cp is the centroid of the cyclopentadienyl ring C(21)–C(25).

bond angles of 120(2)° for Os(1)C(13)C(14) and 122(2)° for C(13)C(14)C(15), is typical for the undistorted olefinic moiety.

The non-equivalence of the distances between the Mn atom and the olefinic carbon atoms (Mn–C(13) 2.08(3) Å and Mn–C(14) 2.28(2) Å) probably reflects asymmetric character of the π-bonding of Mn with the C(13)=C(14) double bond. The MnC(13)C(14) and MnC(14)C(13) bond angles are also quite different, 78(1)° and 63(1)°, respectively. Similar asymmetry was found recently [18] for a $\sigma:\eta^2$-coordinated olefinic group in the dimanganese complex.

The C(12)O(12) carbonyl bridge is also slightly asymmetrical: the Mn–C(12) and Os(1)–C(12) bond lengths are 1.89(3) Å and 2.16(3) Å, the Os(1)C(12)O(12) and MnC(12)O(12) bond angles being equal to 131(2)° and 143(2)°, respectively. The C(12) atom occupies one of the equatorial positions of the Os(1) atom distorted octahedron (see above), although it deviates significantly (0.45(3) Å) from the plane of the osmium triangle.

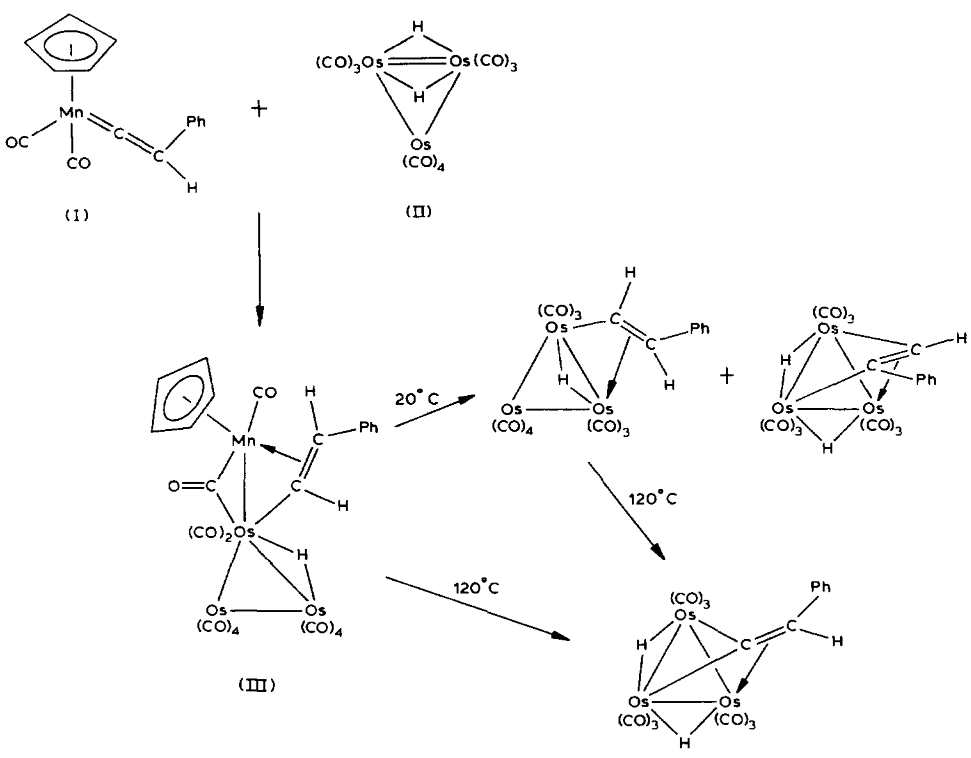
The unique feature of the structure of III is that both bridged fragments, MnOs(1)C(12) and MnOs(1)C(13), are essentially coplanar (the dihedral angle is 173°), and their planes are almost perpendicular to that of the osmium triangle: the Os(1)Os(2)Os(3)/MnOs(1)C(12) and Os(1)Os(2)Os(3)/MnOs(1)C(13) dihedral angles are 96° and 98°, respectively.

All the other geometrical parameters of III are quite unexceptional. The solvating dioxane molecules, being in a "chair" conformation, occupy cavities in the crystal packing and have no short contacts with the molecules of III.

The structural data presented above show that complex III has a peculiar geometry. It belongs to the rare class of "spiked" clusters. The coordination environment of both the Mn and Os(1) atoms displays some interesting features. Their coordination spheres are overcrowded with ligands of very different nature. The Mn–Os(1) bond is bridged by a CO group, which is rather unusual for cymantrene derivatives. Finally, the mode of bonding of the CH=CHPh group with the Mn–Os(1) system by means of a σ-bond with Os(1) and η-coordination with Mn is quite unexpected. The existence of a μ_2-$\sigma:\eta$-coordinated vinyl group was found earlier in a few homometallic molecules, e.g., in $HOs_3(\mu\text{-}CR{=}CHR)(CO)_{10}$ (R = H [14], Ph [15]), $Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7$ [18] and $Cp_2Mo_2(\mu\text{-}CH{=}CHPh)(O)(CO)$ [19], but only two examples of heteronuclear complexes with such ligands have recently been described: $Cp_2TiW(\mu\text{-}CR{=}CH_2)(\mu\text{-}CO)(CO)$ and $CpPtW(\mu\text{-}CR{=}CH_2)(CO)_2(PMe_3)_2$ ($R = C_6H_4Me$-p) [20].

The knowledge of the structure of III enables us to make some speculations concerning the intricate process of formation of this complex and the driving force of its further transformations according to Scheme 1.

It is probable that the first stage of the formation of III involves coordination of one of the electron-deficient Os atoms with the electron-rich Mn=C bond, followed by intramolecular transfer of a carbonyl group to the neighbouring Os atom and hydrogenation of the α-carbon atom of a vinylidene group. The next stage is bond formation between Mn and the β-carbon of the organic ligand. Thus, the process of formation of III involves transformation of the n-vinylidene into a π-olefinic ligand. Previously it was found [16] that the analogous n-π rearrangement caused by the action of a nucleophilic agent occurs in the reaction of vinylidene complex I with phosphites. For polynuclear mixed-metal compounds such rearrangement has not yet been reported.



SCHEME 1

The easy formation of triosmium clusters with organic ligands in solutions of III in non-polar solvents [2] is apparently due to the significant steric strain in molecule III. Indeed, the presence of the highly strained planar system Os(1)C(12)MnC(13) may be the cause of the low stability of III.

Experimental

Synthesis of $CpMnOs_3(\mu\text{-}CH{=}CHPh)(\mu\text{-}H)(\mu\text{-}CO)(CO)_{11}$ (III)

A solution of 0.250 g (0.9 mmol) of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) and 0.430 g (0.5 mmol) of $H_2Os_3(CO)_{10}$ (II) in 15 ml of CH_2Cl_2 was stirred for 6 h at 20°C. The dark-red zone produced by chromatography of the reaction solution on a silica column with hexane/$CHCl_3$ (2/1) mixture gave, after evaporation and recrystallization from dioxane, 0.354 g (60%) of dark-red crystals of III, m.p. 75–76°C.

X-ray structure analysis

Crystals of III are monoclinic, at 20°C: a 8.998(1), b 12.491(4), c 32.088(8) Å, β 96.55(2)°; V 35830 Å^3, d 2.341 g/cm^3, $Z = 4$; space group $P2_1/c$. The unit cell parameters and intensities of reflections were measured with an automatic four-circle Syntex $P2_1$ diffractometer (λ Mo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 50°$). The absorption correction ($\mu(\lambda$ Mo-$K_\alpha) = 116.7$ cm^{-1}) based on the measurement of the crystal dimensions was applied. The shape of the crystal was approximated to

TABLE 3

COORDINATES OF ATOMS ($\times 10^5$; for Os$\times 10^4$) AND THEIR TEMPERATURE FACTORS [a]

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
Os(1)	69571(10)	14611(9)	32224(3)	4.61(3)	C(10)	10370(31)	−52(27)	3484(10)	10(1)
Os(2)	70307(10)	−8145(9)	31593(4)	5.17(3)	C(11)	9477(34)	3644(23)	3454(10)	8(1)
Os(3)	96556(9)	2809(9)	29368(3)	4.29(3)	C(12)	7191(25)	3145(22)	3087(8)	6.2(9)
Mn	7895(4)	3292(3)	3661(1)	5.8(1)	C(13)	7956(30)	1697(21)	3844(8)	6.3(9)
O(1)	4046(14)	1458(19)	3584(6)	9.0(8)	C(14)	9527(25)	2002(18)	3923(8)	4.8(8)
O(2)	5304(18)	1529(20)	2325(6)	9.2(8)	C(15)	10273(26)	2207(20)	4355(8)	5.4(8)
O(3)	7886(23)	−588(16)	4102(7)	8.7(8)	C(16)	9635(31)	1832(25)	4718(9)	7(1)
O(4)	6292(20)	−928(20)	2196(6)	9.2(8)	C(17)	10409(38)	2024(32)	5145(12)	11(2)
O(5)	3737(21)	−1120(21)	3289(8)	12(1)	C(18)	11806(38)	2599(32)	5168(12)	11(1)
O(6)	8068(23)	−3118(16)	3188(7)	9.7(8)	C(19)	12417(36)	2889(35)	4794(10)	11(2)
O(7)	10638(19)	−1974(16)	2674(7)	8.7(8)	C(20)	11607(32)	2679(28)	4397(10)	9(1)
O(8)	12357(19)	1583(18)	2754(7)	9.2(8)	C(21)	6544(42)	4722(29)	3634(10)	10(1)
O(9)	8288(19)	850(15)	2028(5)	6.5(6)	C(22)	7873(48)	4906(29)	3916(11)	11(2)
O(10)	11017(20)	−235(18)	3838(6)	8.3(7)	C(23)	7862(46)	4125(27)	4236(10)	10(1)
O(11)	10638(27)	3944(19)	3335(7)	10.7(9)	C(24)	6550(43)	3496(26)	4176(10)	10(1)
O(12)	6894(18)	3644(15)	2770(5)	6.7(8)	C(25)	5646(31)	3899(28)	3773(10)	9(1)
C(1)	5150(22)	1524(23)	3463(8)	6.0(9)	O_D(11) [b]	5743(26)	802(21)	4809(7)	11(1)
C(2)	5947(32)	1479(25)	2635(9)	8(1)	C_D(11) [b]	6508(41)	181(36)	5130(11)	11(2)
C(3)	7442(22)	−577(18)	3696(12)	8(1)	C_D(12) [b]	4490(43)	279(43)	4565(13)	14(2)
C(4)	6571(22)	−852(22)	2543(9)	6.5(9)	O_D(21) [c]	8437(56)	1315(43)	905(16)	24(2)
C(5)	4991(28)	−1017(24)	3253(9)	7(1)	O_D(22) [c]	5375(53)	1275(43)	601(15)	24(2)
C(6)	7756(24)	−2151(29)	3199(10)	9(1)	C_D(21) [c]	7615(95)	2117(82)	1013(31)	28(3)
C(7)	10276(19)	−1105(28)	2780(8)	8(1)	C_D(22) [c]	5938(95)	1934(76)	950(30)	27(3)
C(8)	11377(22)	1086(23)	2827(8)	5.5(8)	C_D(23) [c]	6236(87)	623(65)	435(24)	23(2)
C(9)	8726(25)	657(18)	2346(8)	5.1(8)	C_D(24) [c]	8015(83)	806(62)	495(22)	23(2)

[a] The isotropic temperature factors B_{iso} are given for the atoms of the dioxane molecules. For the other atoms the equivalent isotropic temperature factors $B_{iso}^{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\bar{a}_i \bar{a}_j)$ are listed. [b] Atom of the dioxane molecule in a special position in the centre of symmetry. [c] Atom of the dioxane molecule in a general position.

a polyhedron with six faces. The structure was solved by a standard heavy-atom method. The coordinates of the Os and Mn atoms were determined from the three-dimensional Patterson function, and other non-hydrogen atoms were located by a series of successive electron density syntheses. Together with the cluster molecule, two independent solvating dioxane molecules (one in a special and the other in a general position) were found. The structure was refined by the full-matrix least-squares technique first in the isotropic and then in the anisotropic approximation for all atoms except those of the dioxane molecules. The final R value was 0.046 ($R_w = 0.049$) for 2348 reflections with $F^2 \geqslant 4\ \sigma$. The coordinates of non-hydrogen atoms are listed in Table 3. All calculations were performed with an Eclipse S/200 mini-computer using the locally modified EXTL program package [21].

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