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Trinuclear Osmium and Ruthenium Clusters Containing Ligands Formed by Dehydration and Rearrangement of 1,4-Dihydroxybut-2-yne

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1,4-Dihydroxybut-2-yne, $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, reacts with $\text{Ru}_3(\text{CO})_{12}$ or $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in refluxing cyclohexane to give the products $\text{Ru}_2(\text{CO})_6[\text{C}_4(\text{CH}_2\text{OH})_4]$, $\text{HRu}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$, and $\text{HRu}_3(\text{CO})_9[\text{CHCHC}(\text{CH}_2\text{OH})]$, the clusters being obtained only in very low yield by combinations of dehydration, hydrogen atom transfer, and oxidation of a primary alcohol to an aldehyde. The course of the reaction is better understood for the conversion of $\text{Os}_3(\text{CO})_{10}(\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})$ (formed from the diol and $\text{H}_2\text{Os}_3(\text{CO})_{10}$ at room temperature) at 96 °C to the CHO-substituted μ_3 -allenyl cluster $\text{HOs}_3(\text{CO})_9[\text{CH}_2\text{CC}(\text{CHO})]$ by a decarbonylation at the metal, dehydration of the diol, and a hydrogen atom transfer from carbon to osmium. Finally at 132 °C a 1,2-hydrogen atom shift occurs to give $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$, the crystal and molecular structure of which has been determined by X-ray methods. The compound crystallizes in space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 8.598(9) \text{ \AA}$, $b = 30.328(16) \text{ \AA}$, $c = 6.930(8) \text{ \AA}$, and $\beta = 106.28(8)^\circ$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.066$ for 1598 independent observed reflections. The complex has approximate C_2 symmetry and consists of an isosceles triangular arrangement of osmium atoms, each linked to three carbonyls. The more elongated Os(1)-Os(2) side (2.961 (2) against 2.837 (2) and 2.801 (2) Å for the other two sides) should be bridged by a hydride ligand (not directly located by the X-ray analysis but supported by ^1H NMR evidence) on the basis of some structural features. A formyl-substituted allyl ligand interacts with all the metal atoms, the terminal carbon atoms being σ bonded to two osmium atoms and all the three carbon atoms being involved in a η -bonding system to the third osmium atom.

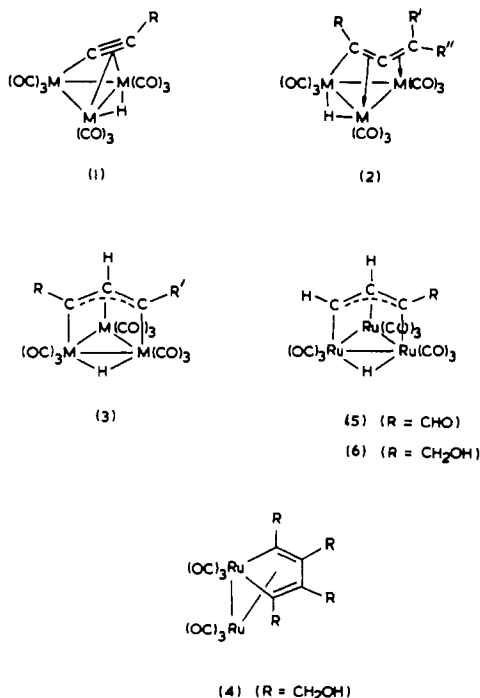
Introduction

The thermal reactions of alkynes with the clusters $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) can give trinuclear clusters containing bridging alkynes, but other products sometimes predominate.¹ Cluster breakdown with alkyne coupling is normal for iron and common for ruthenium except for terminal alkynes which can give μ_3 -alkynyl complexes such as $\text{HRu}_3(\text{CO})_9(\text{C}_2\text{R})$ (**1**), which for $\text{R} = t\text{-Bu}$ is the major product.² Other

$\text{HC}\equiv\text{CCMe}_2\text{OH}$ reacts with $\text{Ru}_3(\text{CO})_{12}$ to give some compound **1** ($\text{R} = \text{CMe}_2\text{OH}$) but mainly dinuclear complexes of formula $\text{Ru}_2(\text{CO})_6(\text{alkyne})_2$.^{3,4} This chemistry and the chemistry with triosmium clusters⁴ could be regarded as normal. However, dihydroxyalkynes behave quite differently; for example, $\text{HOPh}_2\text{CC}\equiv\text{CCPh}_2\text{OH}$ reacts with $\text{Ru}_3(\text{CO})_{12}$ or $\text{Os}_3(\text{CO})_{12}$ to give in good yield the complexes $\text{HM}_3(\text{CO})_9(\text{C}\equiv\text{CCPh}_2\text{OH})$ formed by C-C bond cleavage, with the byproduct being the ketone.⁵ This reaction appears to be general for diols of this form having no α -hydrogen atoms, but in contrast the reaction of $\text{HOCMe}_2\text{C}\equiv\text{CCMe}_2\text{OH}$, for example, with $\text{Fe}_3(\text{CO})_{12}$ leads to the butatriene complex $\text{Fe}_2(\text{CO})_6(\text{Me}_2\text{C}=\text{C}=\text{C}=\text{CMe}_2)$ in which case C-O cleavage has taken place.⁶ A similar reaction occurs with the unsubstituted diol to give, in this case, a poor yield of $\text{Fe}_2(\text{CO})_6(\text{CH}_2=\text{C}=\text{C}=\text{CH}_2)$. We now report the formation of trinuclear clusters of ruthenium and osmium from $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$ which contain fragments of this ligand, and the X-ray crystal structure of one derivative, $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$, has been determined.

Results and Discussion

The diol $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$ reacts with $\text{Ru}_3(\text{CO})_{12}$ in refluxing cyclohexane to give a complex $\text{Ru}_2(\text{CO})_6(\text{alkyne})_2$ (60%) which is sparingly soluble in cyclohexane. The infrared spectrum (KBr) and ^1H and ^{13}C NMR spectra (Table I and Experimental Section) show that the complex is of the known metallacyclopentadiene type **4** formed by alkyne coupling and does not involve bond cleavage within the organic molecule. Chromatography of the yellow cyclohexane filtrate on silica gave low yields of three cluster complexes. One of these was not identified, but the other two are of type **3** and were identified spectroscopically as $\text{HRu}_3(\text{CO})_9(\text{C}_4\text{H}_3\text{O})$, cluster



cluster compounds of types **2** and **3** are also frequently encountered in the reactions of alkynes and dienes with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$). Hydroxy-functionalized alkynes behave rather differently in some cases. The acetylenic alcohol

- (1) Kaesz, H. D.; Humphries, A. P. *Prog. Inorg. Chem.* **1979**, *25*, 146.
- (2) Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169.
- (3) Ermer, S.; Kareplus, R.; Miura, S.; Rosenberg, E.; Tiripicchio, A.; Manotti Lanfredi, A. M. *J. Organomet. Chem.* **1980**, *187*, 81.
- (4) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 828.
- (5) Aime, S.; Milone, L.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1168.
- (6) Victor, R. J. *J. Organomet. Chem.* **1977**, *127*, C25.

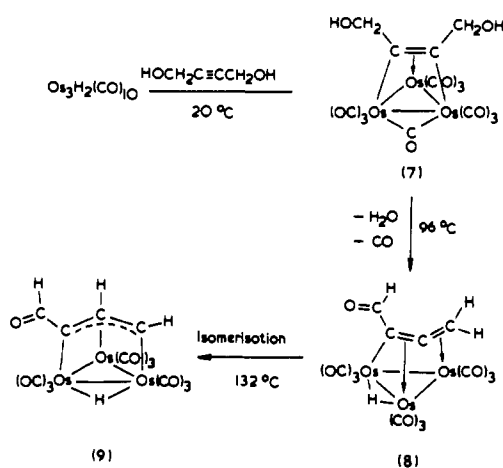
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Table I. Analytical and Spectral Data

compd	$\nu(\text{CO})^a/\text{cm}^{-1}$	δ^b (^1H NMR.)	J/Hz	% C ^c	% H ^c
$\text{Ru}_2(\text{CO})_8[\text{C}_4(\text{CH}_2\text{OH})_4]$ (4)	2085 m, 2054 vs, 2009 vs, 1994 s ^e	5.62 ^d 5.47 ^d (CH ₂)			
$\text{H}^2\text{Ru}_3(\text{CO})_9[\text{CH}^w\text{CH}^x\text{C}(\text{CH}^y\text{O})]$ (5)	2108 m, 2084 vs, 2056 vs, 2040 sh, 2035 s, 2026 s, 2011 mw, 1696 w	9.97 s (H ^y) 8.64 d (H ^w) 7.65 dd (H ^x) -20.3 d (H ^z)	11 11, 3.5 3.5		
$\text{H}^2\text{Ru}_3(\text{CO})_9[\text{CH}^w\text{CH}^x\text{C}(\text{CH}_2^y\text{OH})]$ (6)	2096 m, 2069 vs, 2041 vs, 2024 s, 2013 s, 2009 s	8.5 d (H ^w) 7.3 dd (H ^x) 4.7 s (H ^y) -20.1 d (H ^z)	8 8, 2.5		
$\text{Os}_3(\text{CO})_{10}(\text{HOCH}_2\text{C}_2\text{CH}_2\text{OH})^f$ (7)	2101 w, 2064 vs, 2055 vs, 2019 s, 1998 m, 1843 w (br)	4.36 d } (CH ₂) 3.93 d }	12.5 12.5	18.12 (17.95)	0.66 (0.65)
$\text{H}^2\text{Os}_3(\text{CO})_9[\text{CH}_2^w\text{C}(\text{CH}^y\text{O})]$ (8)	2106 m, 2081 vs, 2053 vs, 2033 vs, 2024 m, 2016 m, 2002 m, 1981 m, 1691 w	9.15 s (H ^y) 4.48 d (H ^w) 3.12 d (H ^x) -22.82 s (H ^z)	1.4 1.4	17.76 (17.53)	0.58 (0.45)
$\text{H}^2\text{Os}_3(\text{CO})_9[\text{CH}^w\text{CH}^x\text{C}(\text{CH}^y\text{O})]^g$ (9)	2106 m, 2080 vs, 2058 vs, 2028 s, 2021 s, 2014 s, 2002 m, 1999 m, 1704 w	9.84 s (H ^y) 8.84 s (H ^x , H ^w) -19.58 s (H ^z)		18.19 (17.53)	0.79 (0.45)

^a Recorded in cyclohexane except 4 which is in KBr. ^b Recorded in CDCl₃ at ambient temperature unless stated otherwise. ^c Calculated figures in parentheses. ^d Recorded in CD₃OD; OH of complex exchanging with solvent. ^e KBr disk. ^f $\nu(\text{OH}) = 3635 \text{ cm}^{-1}$ (cyclohexane); NMR at -30°C ; spectrum coalesced at room temperature. ^g ^1H NMR (CD₃COCD₃): δ 8.99 s (H^w, H^x), 9.78 s (H^y), -19.78 s (H^z). ^1H NMR (C₆D₅CD₃): δ 8.00 d (H^w), 7.65 d (H^x) ($J_{\text{wx}} = 7.5 \text{ Hz}$), 9.15 s (H^y), -19.66 d (H^z).

Scheme I



5 (R = CHO), and as $\text{HRu}_3(\text{CO})_9(\text{C}_4\text{H}_5\text{O})$, cluster **6** (R = CH₂OH). Both can be clearly identified as the "pseudoallyl" type compounds shown. The formyl substituent in **5** is identified by a ^1H NMR singlet at δ 9.97 and a $\nu(\text{CO})$ absorption at 1696 cm^{-1} .

Mainly because of the low yields of these trinuclear clusters, the chemical routes to them could not be established. The synthesis of a cluster containing the unmodified diol ligand seemed desirable to enable a study of its subsequent transformations. Indeed we were able to synthesize such a cluster for osmium. Thus $\text{Os}_3(\text{CO})_{10}(\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})$, compound **7** (Scheme I), is obtained in adequate yield (25%) from the room-temperature reaction of the diol with $\text{H}_2\text{Os}_3(\text{CO})_{10}$, a particularly reactive and useful precursor to triruthenium clusters. The bridging CO absorption at 1843 cm^{-1} indicates that compound **7** does not adopt a structure like that found for $\text{Os}_3(\text{CO})_{10}(\text{PhC}\equiv\text{CPh})$ with no bridging CO⁷ but rather the more commonly found structure shown in Scheme I. As expected the CH₂ protons are diastereotopic and give an AB (^1H NMR) quartet at -30°C which coalesces to a broad singlet at room temperature. Flipping of the alkyne as it

rotates with respect to the Os₃ triangle is a mechanism to account for the coalescence of the AB quartet as proposed for other 4e-donating μ_3 -alkynes.^{4,8}

It is unlikely that **7** could be synthesized by direct reaction of the alkyne with $\text{Os}_3(\text{CO})_{12}$ because at the temperatures required for this reaction the complex decarbonylates and dehydrates. Thus at 96°C in heptane it converts in 50% isolated yield to $\text{HOs}_3(\text{CO})_9[\text{CH}_2\text{CC}(\text{CHO})]$ (**8**). The mass spectrum and analytical data confirm that H₂O and CO have been lost from compound **7**. The ^1H NMR spectrum is consistent with a formyl-substituted μ_3 -allenyl ligand formed by a dehydration and a hydrogen atom transfer from carbon to osmium. The formyl group is identified by a ^1H NMR singlet (δ 9.15) and $\nu(\text{CO})$ at 1691 cm^{-1} (see Table I). The complex relates directly to $\text{HOs}_3(\text{CO})_9(\text{CH}_2\text{CCMe})^9$ and $\text{HRu}_3(\text{CO})_9(\text{MeCHCCEt})$; the X-ray structure of the triruthenium cluster is known.¹⁰

Finally at 132°C compound **8** isomerizes to $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$ (**9**) by a 1,2-hydrogen shift. Compound **9** is in most ways spectroscopically analogous to the "pseudo allyl" ruthenium cluster **5** and certainly its formation from **8** is expected. There are, however, certain anomalies. Notably there are only two ^1H NMR singlets in ratio 2:1 apart from the hydride signal at high field. The singlet at δ 9.84 for the CHO group compares with that at δ 9.97 for the ruthenium compound **5**, but the other two hydrogen atoms give a singlet at δ 8.84 in CDCl₃. A singlet is also observed at -60°C and in CD₃COCD₃ over a range of temperatures. It seemed strange for accidental coincidence of signals to persist over all these conditions especially as the terminal CH group of the allyl normally resonates at lower field than the central CH group. For clarification of this point a crystal structure determination was carried out. This clearly showed that all the hydrogen atoms are nonequivalent, and finally we showed for a C₆D₅CD₃ solution that an AB quartet ($J = 7.5 \text{ Hz}$) could be obtained. It is simply accidental coincidence and not dynamical exchange that gives the singlet in CDCl₃ and CD₃COCD₃ solutions.

(7) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172.

(8) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123.

(9) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

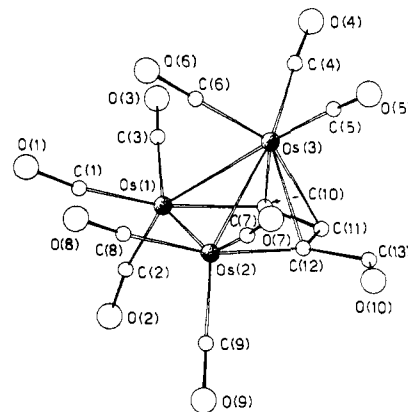
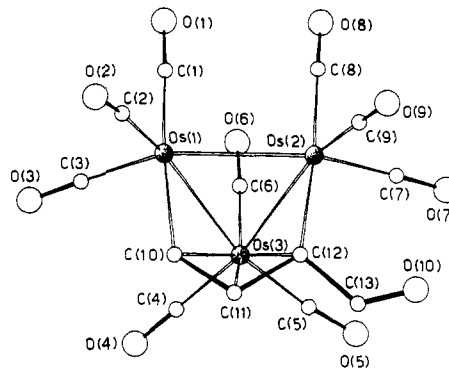
(10) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221.

Table II. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Os(1)	2079 (2)	4230 (1)	3188 (2)
Os(2)	4999 (2)	3664 (1)	4351 (2)
Os(3)	2539 (2)	3510 (1)	793 (2)
O(1)	4121 (38)	5018 (11)	2687 (52)
O(2)	971 (39)	4614 (12)	6687 (51)
O(3)	-923 (36)	4563 (12)	77 (54)
O(4)	-420 (35)	3527 (14)	-2850 (53)
O(5)	4043 (49)	2763 (12)	-1031 (62)
O(6)	4364 (40)	4243 (10)	-688 (42)
O(7)	7428 (33)	3091 (11)	3056 (45)
O(8)	7163 (38)	4424 (13)	3962 (66)
O(9)	6632 (36)	3505 (12)	8706 (56)
O(10)	5124 (40)	2548 (10)	4423 (58)
C(1)	3355 (54)	4710 (15)	3060 (78)
C(2)	1492 (45)	4492 (16)	5247 (83)
C(3)	253 (54)	4447 (13)	1194 (76)
C(4)	760 (62)	3524 (17)	-1572 (57)
C(5)	3378 (56)	3043 (15)	-416 (62)
C(6)	3678 (50)	3953 (14)	-95 (69)
C(7)	6512 (38)	3309 (13)	3655 (68)
C(8)	6372 (42)	4155 (15)	4198 (86)
C(9)	6023 (38)	3569 (14)	7021 (47)
C(10)	874 (36)	3636 (13)	2738 (57)
C(11)	1500 (41)	3195 (14)	3152 (57)
C(12)	3339 (46)	3167 (14)	3792 (56)
C(13)	3798 (51)	2688 (15)	3824 (77)

Structure of $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$

The crystal structure consists of discrete $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$ molecules, mutually separated by normal van der Waals distances. Two views of the molecule, with the system for labeling atoms, are shown in Figures 1 and 2. Bond distances and angles in it are contained in Table IV. The complex, having approximate C_s (*m*) symmetry (if the substituent in the allyl group is ignored), can be considered deriving by substituting three (one for each metal) axial carbonyls in $\text{Os}_3(\text{CO})_{12}$ with a hydride and a formyl-substituted allyl ligands, which provide the total of six electrons required by the $\text{Os}_3(\text{CO})_9$ group. The three osmium atoms define an isosceles triangle in which the Os(1)–Os(2) side (2.961 (2)

**Figure 1.** Perspective view of the complex $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{C-HO})]$ with the system of labeling atoms.**Figure 2.** View of the complex $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$ showing the nearly C_s symmetry.

Å) is much longer than the other two Os(1)–Os(3) and Os(2)–Os(3) sides (2.837 (2) and 2.801 (2) Å). The cluster is bound to nine carbonyls (three for each metal) and to a 1-formylallyl ligand through all the metals. The nine carbonyls are all terminal (the Os–C–O angles ranging from 171 to 178°), three (one for each metal) being axial and six (two for

Table III. Anisotropic Thermal Parameters^a ($\times 10^4$) with Esd's in Parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	250 (10)	410 (10)	420 (10)	20 (10)	10 (10)	40 (10)
Os(2)	200 (10)	470 (10)	400 (10)	20 (10)	-40 (10)	20 (10)
Os(3)	220 (10)	450 (10)	420 (10)	-40 (10)	-20 (10)	-50 (10)
O(1)	550 (200)	810 (250)	860 (260)	30 (200)	140 (180)	10 (180)
O(2)	730 (230)	960 (270)	640 (210)	-250 (200)	290 (180)	190 (190)
O(3)	560 (190)	1110 (260)	880 (250)	300 (210)	-160 (180)	480 (180)
O(4)	430 (160)	1710 (420)	790 (220)	-80 (240)	-100 (170)	-170 (210)
O(5)	1260 (340)	690 (230)	1100 (350)	-230 (230)	590 (290)	170 (230)
O(6)	710 (220)	550 (180)	420 (160)	-70 (140)	20 (150)	-270 (170)
O(7)	380 (150)	780 (230)	720 (210)	120 (180)	110 (150)	50 (160)
O(8)	320 (170)	1010 (280)	1850 (410)	430 (280)	140 (210)	70 (180)
O(9)	330 (170)	1380 (280)	910 (270)	160 (230)	70 (180)	110 (180)
O(10)	700 (220)	610 (210)	1680 (300)	520 (200)	430 (210)	230 (180)
C(1)	460 (280)	470 (270)	940 (390)	-500 (270)	170 (280)	100 (230)
C(2)	210 (200)	910 (300)	1520 (430)	580 (310)	-390 (240)	-150 (200)
C(3)	700 (270)	140 (210)	910 (390)	200 (240)	20 (270)	30 (200)
C(4)	800 (370)	1070 (400)	390 (210)	-220 (230)	310 (260)	70 (300)
C(5)	730 (280)	520 (280)	410 (230)	-140 (220)	40 (210)	-260 (240)
C(6)	340 (250)	590 (270)	620 (310)	-370 (250)	-70 (220)	-120 (210)
C(7)	120 (160)	480 (260)	670 (320)	130 (240)	-10 (190)	70 (170)
C(8)	110 (170)	690 (310)	1630 (470)	390 (290)	-50 (220)	-130 (180)
C(9)	230 (180)	730 (330)	460 (180)	330 (190)	-10 (140)	230 (190)
C(10)	110 (150)	570 (250)	530 (240)	160 (190)	130 (150)	130 (160)
C(11)	340 (200)	650 (270)	540 (240)	90 (210)	410 (190)	-50 (190)
C(12)	450 (230)	610 (290)	250 (230)	140 (200)	100 (190)	230 (210)
C(13)	490 (240)	560 (300)	750 (370)	70 (270)	70 (240)	10 (220)

^a In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})]$.

each metal) equatorial. Since it was impossible to locate the hydride directly from the X-ray structural analysis, its position, bridging the Os(1)–Os(2), may reliably be inferred from its effects on the geometry of the complex, as pointed out by Churchill et al.¹¹

A single hydride bridging a side of the cluster should produce an elongation of the bridged side with respect to the nonbridged and a relevant displacement of the equatorial carbonyls in such a way to increase the angles Os(2)–Os(1)–C(2) and Os(1)–Os(2)–C(9). Both these effects can be observed in the complex. The Os(1)–Os(2) side is longer than the other two, and the Os(2)–Os(1)–C(2) and Os(1)–Os(2)–C(9) angles are of 116 and 120°, much larger than any other equatorial cis Os–Os–CO angle in the molecule (the range of other such angles is 94–106°).

The substituted allyl ligand is in a nearly symmetrical way bonded to all the metals: the terminal C(10) and C(12) atoms are σ bonded to the Os(1) and Os(2) atoms (Os(1)–C(10) = 2.06 (2), Os(2)–C(12) = 2.04 (2) Å; these two carbon atoms together with the central C(11) atom form a C₃ system η bonded to the Os(3) atom and nearly equidistant from it (Os(3)–C(10) = 2.26 (2), Os(3)–C(11) = 2.28 (2), Os(3)–C(12) = 2.25 (2) Å).

The C(10), C(11), and C(12) atoms form with Os(1) and Os(2) atoms a quasi-planar pentaatomic heterocycle, inclined at 50° to the cluster triangle. The C(10), C(11), C(12), Os(1), Os(2), C(13), O(10), and Os(3) atoms are displaced from the mean plane passing through this pentaatomic ring by 0.04, –0.04, 0, 0, 0.13, 0.07, and 1.84 Å, respectively, indicating that the aldehydic group is nearly coplanar both with the allyl ligand and with the heterocycle.

The bonding of the allyl ligand in the present complex is closely similar to that found in HRu₃(CO)₉(CMeCHCET)¹² and in HRu₃(CO)₉(C₆H₅CC₆H₄).¹³

In the two butterfly tetranuclear Ru₄(CO)₁₀(C₁₂H₁₆)¹⁴ and (Cp)NiRu₃(CO)₈(CMeCHCET)¹⁵ the allyl ligand is bound to the metal cluster, forming two π bonds with the hinge atoms through the terminal carbon atoms and a double η -bonding system with the wings atoms through all the three carbon atoms.

The CHO group does not interact with any metal atom.

Experimental Section

Analytical and spectral data are given in Table I. Parent molecular ions were observed for all the cluster hydride compounds in the mass spectra.

Syntheses

Action of HOCH₂C≡CCH₂OH on Ru₃(CO)₁₂. A solution of Ru₃(CO)₁₂ and the diol (3 mol/Ru₃) was refluxed in cyclohexane until all the parent carbonyl compound was consumed (5 h). The dinuclear compound Ru₂(CO)₆[C₄(CH₂OH)₄] was precipitated as a yellow solid (60%). ¹H NMR data are in Table I; ¹³C NMR (CD₃OD): δ 69.1, 57.4 (CH₂, triplets in uncoupled spectrum); 171.4, 131.4 (C–CH₂); 199.9, 198.0 (CO). Chromatography (SiO₂) of the filtered solution gave an unknown compound (1%), HRu₃(CO)₉[CHCHC(CHO)] (7%), and HRu₃(CO)₉[CHCH(CH₂OH)] (4%) as yellow solids. These two cluster hydrides were also obtained from a similar reaction with H₄Ru₄(CO)₁₂.

Action of HOCH₂C≡CCH₂OH on H₂O₃(CO)₁₀. A suspension of H₂O₃(CO)₁₀ (0.520 g) and the diol (0.188 g) in methanol (25 mL) was shaken for 15 min and then kept at 20 °C for 20 h. Removal of solvent and TLC (SiO₂, eluant ether/toluene mixtures) gave more

Table IV. Bond Distances (Å) and Angles (Deg)

(i) In the Coordination Sphere of the Osmium Atoms			
Os(1)–Os(2)	2.961 (2)	Os(2)–C(9)	1.83 (1)
Os(1)–Os(3)	2.837 (2)	Os(2)–C(12)	2.04 (2)
Os(2)–Os(3)	2.801 (2)	Os(3)–C(4)	1.90 (2)
Os(1)–C(1)	1.84 (2)	Os(3)–C(5)	1.89 (2)
Os(1)–C(2)	1.82 (2)	Os(3)–C(6)	1.86 (2)
Os(1)–C(3)	1.89 (2)	Os(3)–C(10)	2.26 (2)
Os(1)–C(10)	2.06 (2)	Os(3)–C(11)	2.28 (2)
Os(2)–C(7)	1.85 (2)	Os(3)–C(12)	2.25 (2)
Os(2)–C(8)	1.92 (2)		
Os(2)–Os(1)–Os(3)	57.7 (1)	C(9)–Os(2)–Os(1)	120 (1)
Os(3)–Os(2)–Os(1)	58.9 (1)	C(12)–Os(2)–Os(1)	83 (1)
Os(1)–Os(3)–Os(2)	63.4 (1)	C(4)–Os(3)–C(5)	87 (1)
Os(2)–Os(1)–C(1)	90 (1)	C(4)–Os(3)–C(6)	94 (1)
Os(2)–Os(1)–C(2)	116 (1)	C(4)–Os(3)–C(10)	91 (1)
Os(2)–Os(1)–C(3)	150 (1)	C(4)–Os(3)–C(11)	104 (1)
Os(2)–Os(1)–C(10)	83 (1)	C(4)–Os(3)–C(12)	140 (1)
Os(3)–Os(1)–C(1)	113 (1)	C(4)–Os(3)–Os(1)	106 (1)
Os(3)–Os(1)–C(2)	155 (1)	C(4)–Os(3)–Os(2)	169 (1)
Os(3)–Os(1)–C(3)	94 (1)	C(5)–Os(3)–C(6)	95 (1)
Os(3)–Os(1)–C(10)	52 (1)	C(5)–Os(3)–C(10)	141 (1)
C(1)–Os(1)–C(2)	90 (1)	C(5)–Os(3)–C(11)	106 (1)
C(1)–Os(1)–C(3)	94 (1)	C(5)–Os(3)–C(12)	90 (1)
C(1)–Os(1)–C(10)	165 (1)	C(5)–Os(3)–Os(1)	166 (1)
C(2)–Os(1)–C(3)	94 (1)	C(5)–Os(3)–Os(2)	103 (1)
C(2)–Os(1)–C(10)	105 (1)	C(6)–Os(3)–C(10)	124 (1)
C(3)–Os(1)–C(10)	85 (1)	C(6)–Os(3)–C(11)	152 (1)
Os(3)–Os(2)–C(7)	95 (1)	C(6)–Os(3)–C(12)	126 (1)
Os(3)–Os(2)–C(8)	114 (1)	C(6)–Os(3)–Os(1)	79 (1)
Os(3)–Os(2)–C(9)	153 (1)	C(6)–Os(3)–Os(2)	80 (1)
Os(3)–Os(2)–C(12)	53 (1)	C(10)–Os(3)–C(11)	37 (1)
C(7)–Os(2)–C(8)	87 (1)	C(10)–Os(3)–C(12)	67 (1)
C(7)–Os(2)–C(9)	90 (1)	C(10)–Os(3)–Os(1)	46 (1)
C(7)–Os(2)–C(12)	91 (1)	C(10)–Os(3)–Os(2)	84 (1)
C(7)–Os(2)–Os(1)	150 (1)	C(11)–Os(3)–C(12)	39 (1)
C(8)–Os(2)–C(9)	93 (1)	C(11)–Os(3)–Os(1)	76 (1)
C(8)–Os(2)–C(12)	166 (1)	C(11)–Os(3)–Os(2)	78 (1)
C(8)–Os(2)–Os(1)	91 (1)	C(12)–Os(3)–Os(1)	83 (1)
C(9)–Os(2)–C(12)	101 (1)	C(12)–Os(3)–Os(2)	46 (1)
(ii) In the Carbonyl Groups			
O(1)–C(1)	1.21 (3)	O(6)–C(6)	1.19 (3)
O(2)–C(2)	1.26 (3)	O(7)–C(7)	1.19 (3)
O(3)–C(3)	1.14 (3)	O(8)–C(8)	1.10 (3)
O(4)–C(4)	1.14 (3)	O(9)–C(9)	1.15 (3)
O(5)–C(5)	1.17 (3)		
Os(1)–C(1)–O(1)	171 (2)	Os(3)–C(6)–O(6)	178 (2)
Os(1)–C(2)–O(2)	171 (2)	Os(2)–C(7)–O(7)	175 (2)
Os(1)–C(3)–O(3)	174 (2)	Os(2)–C(8)–O(8)	174 (2)
Os(3)–C(4)–O(4)	172 (2)	Os(2)–C(9)–O(9)	178 (2)
Os(3)–C(5)–O(5)	173 (4)		
(iii) In the Organic Ligand			
C(10)–C(11)	1.44 (3)	C(12)–C(13)	1.50 (3)
C(11)–C(12)	1.52 (3)	C(13)–O(10)	1.18 (3)
Os(1)–C(10)–Os(3)	82 (1)	C(13)–C(12)–Os(3)	118 (2)
C(11)–C(10)–Os(1)	130 (2)	C(13)–C(12)–C(11)	108 (2)
C(11)–C(10)–Os(3)	72 (2)	Os(2)–C(12)–Os(3)	81 (1)
C(12)–C(11)–Os(3)	69 (2)	Os(2)–C(12)–C(11)	129 (2)
C(12)–C(11)–C(10)	114 (2)	Os(3)–C(12)–C(11)	71 (2)
Os(3)–C(11)–C(10)	71 (2)	O(10)–C(13)–C(12)	125 (3)
C(13)–C(12)–Os(2)	123 (2)		

than four bands, several still mixtures, from which Os₃(CO)₁₀(HOCH₂C≡CCH₂OH) (0.144 g, 25%) was isolated as orange crystals. The only other complex to be obtained pure was HO₃(CO)₁₀(OH) (0.025 g), characterized by elemental analysis and infrared and ¹H NMR spectra.

Thermolysis of Os₃(CO)₁₀(HOCH₂C≡CCH₂OH). A solution of the alkyne complex (0.072 g) in heptane (20 mL) was heated under reflux for 90 min under nitrogen. Removal of solvent and then TLC (SiO₂, elution with toluene/pentane, 1:1 by volume) gave minor bands containing no more than 0.005 g and a yellow band that gave HO₃(CO)₉[CH₂CC(CHO)] as yellow crystals (0.034 g).

Thermolysis of HO₃(CO)₉[CH₂CC(CHO)]. A solution of the complex (0.015 g) in petroleum/ether (bp 120–160 °C) was heated

- Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
- Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E.; Milone, L.; Valle, M. J. *Chem. Soc., Chem. Commun.* **1972**, 545.
- Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 633.
- Bruce, M. I.; Cairns, M. A.; Green, M. J. *Chem. Soc., Dalton Trans.* **1972**, 1293.
- Osella, D.; Sappa, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *Inorg. Chim. Acta* **1979**, *34*, L289.

under reflux for 2.5 h. Removal of the solvent and then TLC (SiO_2) gave $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$ (0.007 g) as yellow crystals. The same compound was also obtained by direct treatment of $\text{Os}_3(\text{C}-\text{O})_{10}(\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})$ in refluxing petroleum ether (bp 120–160 °C).

X-ray Data Collection

The yellow crystals of the complex $\text{HOs}_3(\text{CO})_9[\text{CHCHC}(\text{CHO})]$ were of poor quality and mostly twinned. A very thin, roughly shaped fragment, cleaved from a larger crystal, having approximate dimensions ca. $0.03 \times 0.10 \times 0.30$ mm, was found untwinned and used for the structure determination. It was mounted on a glass fiber on a eucentric goniometer head. Preliminary rotation and Weissenberg photographs yielded approximate cell dimensions and indicated C_{2h} Laue symmetry and the monoclinic $P2_1/n$ space group from the systematic absences. The crystal was transferred onto a Siemens AED single-crystal diffractometer mounted with the c axis along the ϕ axis of the diffractometer. The setting of 17 reflections with 2θ greater than 20° were determined with use of the Mo $K\alpha$ radiation and used to calculate the refined cell parameters. The crystal data are as follows: $\text{C}_{13}\text{H}_4\text{O}_{10}\text{Os}_3$, mol wt 890.77, monoclinic, $a = 8.598$ (9) Å, $b = 30.328$ (16) Å, $c = 6.930$ (8) Å, $\beta = 106.28$ (8)°, $V = 1735$ (3) Å³, $Z = 4$, $\rho(\text{calcd}) = 3.411$ g/cm³, $\mu(\text{Mo } K\alpha) = 220.05$ cm⁻¹, space group $P2_1/n$.

A complete set of intensity data (hkl , $\bar{h}kl$) were collected, at room temperature, with θ in the range $3\text{--}23^\circ$ on the same diffractometer using the niobium-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at a takeoff angle of 4° . The pulse height discriminator was set to accept 90% of the Mo $K\alpha$ peak radiation. The $\theta/2\theta$ scan technique was used with a variable scan rate ranging from 2.5 to $10^\circ/\text{min}$. Scan range was ± 0.5 from peak center. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. Its variation in intensity over the time required to collect data was less than 3%. For intensities and background the five-point technique¹⁶ was used. A total of 2419 independent reflections were measured: 1598 of these, for which $I > 2\sigma(I)$ ($\sigma(I) = [\text{total counts} + (0.05 \times \text{intensity})^2]^{1/2}$) were considered observed and employed in the analysis. Intensities were corrected for Lorentz and polarization factors. Although absorption is undoubtedly important in this structure, an absorption correction was not made because the very small and irregular size of the crystal prevents morphological measurements of

it. Data were placed on an approximate absolute scale by means of a Wilson plot, which also yielded the overall temperature factor.

Structure Determination and Refinement

Crude atomic coordinates of the three osmium atoms were determined from a Patterson map. A difference Fourier map calculated with phases of the three metal atoms revealed the positions of all other nonhydrogen atoms. Refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs¹⁷ with first isotropic and then anisotropic thermal parameters. No attempt was made to localize hydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; unit weights were used in the first cycles of refinement, the weight calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 0.2089$ and $g = 0.005$ was chosen in the final cycles. The refinement converged to a discrepancy factor $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ equal to 0.066 and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ equal to 0.082 (observed reflections only).

The analytical scattering factors for neutral osmium, oxygen, carbon, and hydrogen were used throughout the analysis; both the real and imaginary components of anomalous dispersion were included for osmium atom.¹⁸ The atomic fractional coordinates and the thermal parameters for nonhydrogen atoms are given in Table II and III, respectively.

All the calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy, with financial support from the University of Parma.

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Registry No. 4, 76879-88-4; 5, 76900-28-2; 6, 76879-87-3; 7, 76879-86-2; 8, 76879-85-1; 9, 76879-84-0; $\text{HOs}_3(\text{CO})_{10}(\text{OH})$, 23064-66-6; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, 34438-91-0; $\text{H}_2\text{Os}_3(\text{CO})_{10}$, 41766-80-7; $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, 110-65-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

(16) Hoppe, W. *Acta Crystallogr., Sect. A* 1969, A25, 67.

(17) Sheldrick, G. M. "System of Computing Programs"; University of Cambridge: Cambridge, 1976.

(18) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.