Reactions of Alkynes with $[Os_3(CO)_{11}(NCCH_3)]$: the Crystal Structures of $[Os_3(CO)_9(C_3H_2OH)H]$ and $[Os_3(CO)_9(C_3H_2OCH_3)H]$ †

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The reaction of $[Os_3(CO)_{11}(NCCH_3)]$ with hydrous C_2H_2, $CH_3C{\equiv}CH$, or $PhC{\equiv}CH$ yields, as the major product, $[Os_3(CO)_9(RC_3H_2O)H]$ (R = H, CH_3, or C_6H_5). The backbone of the organic ligand, an allyl alcohol, is formed from an alkyne molecule and a CO ligand from the cluster. It bonds to a face of the triangular cluster through two σ bonds and one π-allyl bond. The complexes exist in two isomeric forms which have not been separated. The complex $[Os_3(CO)_9(C_3H_2OH)H]$ crystallizes in space group *Pbca* with $a = 16.291(5)$, $b = 16.861(5)$, $c = 12.234(3)$ Å, and $Z = 8$. Its structure has been solved by a combination of direct methods and Fourier-difference techniques, and refined by full-matrix least squares to an *R* of 0.060 for 1 327 diffractometer data. Both isomers co-crystallize in this complex, and the structure shows that the organic ligand is disordered, preventing an assessment of the nature of the isomers. Conversion of the allyl alcohol ligand into an allyl methyl ether has allowed the determination of one of the isomers. Thus $[Os_3(CO)_9(C_3H_2OCH_3)H]$ crystallizes in space group $P2_1/n$ with $a = 6.975(3)$, $b = 30.960(6)$, $c = 8.695(4)$ Å, $\beta = 107.62(2)°$, and $Z = 4$. Its structure has been solved by a combination of direct methods and Fourier-difference techniques, and refined by full-matrix least squares to an *R* of 0.053 for 1 671 diffractometer data. The two isomers in the $[Os_3(CO)_9(RC_3H_2O)H]$ molecules are thought to be due to restricted rotation about the C–O bond of the alcohol, giving rise to two possible orientations for the O–H proton. Only one of these orientations is accessible to the allyl methyl ether derivative.

THE two preparative routes to alkyne derivatives of triosmium clusters involve either direct thermal reaction of $[Os_3(CO)_{12}]$ with RCCR′ in refluxing solvent,[1-3] or the reaction of an activated cluster with RCCR′ at ambient temperature.[4,5] These reactions have received considerable attention and have led to a rich and complex area of chemistry.

The thermal reactions yield a variety of products depending upon the experimental conditions and the alkyne used. In the reactions of phenylacetylene, for example, the products obtained include $[Os_3(CO)_{10}(PhCCH)]$ (1), $[Os_3(CO)_{10}(PhCCH)_2]$ (2), $[Os_3(CO)_9(PhCCH)_2]$ (3), and $[Os_3(CO)_7(PhCCH)_3]$ (4).[3] The thermal reactions often proceed with metallocycle and carbon–carbon bond formation.

When the activated cluster $[Os_3(CO)_{10}H_2]$ is employed the reactions of alkynes lead to a simpler array of products.[4] For phenylacetylene the main species isolated are $[Os_3(CO)_{10}(PhHCCCH_3)_3H]$ (5) and $[Os_3(CO)_{10}(C_2Ph)H]$ (6). The formation of these, and the products obtained with other alkynes, is thought to proceed *via* insertion to form a vinyl complex. The reaction may either terminate with the vinyl complex (5), or the displacement of an alkene may allow further reaction with another alkyne as in (6). For certain alkynes metallocycle formation is observed.[4]

The reaction of alkynes with the bis(acetonitrile) derivative of triosmium dodecacarbonyl, $[Os_3(CO)_{10}(NCCH_3)_2]$, leads simply to $[Os_3(CO)_{10}(alkyne)]$ molecules.[5]

In general alkynyls have been observed to behave as three- or four-electron donors on triosmium clusters. For mononuclear compounds, however, alkynes often behave as two-electron donors,[6] and the alkyne derivatives are often obtained by displacement of an acetonitrile ligand. The reaction of $[Os_3(CO)_{11}(NCCH_3)]$ with terminal alkynes gives $[Os_3(CO)_9(RC_3H_2O)H]$ as the major product. Yields as high as 70% are obtained when the reaction is performed in the presence of water. The ligand RC_3H_2O is best described as an allyl alcohol. The preparation of these compounds and the crystal structures of $[Os_3(CO)_9(C_3H_2OH)H]$ (7) and its methyl ether derivative, $[Os_3(CO)_9(C_3H_2OCH_3)H]$ (8), are described.

EXPERIMENTAL

All operations were performed under a nitrogen atmosphere unless otherwise indicated. Solvents were distilled from an appropriate drying agent and stored under nitrogen. ‘ Wet ’ CH_2Cl_2 was prepared by adding a small volume of water to *ca.* 100 cm³ of solvent. Phenylacetylene was passed through a short alumina column prior to use. Propyne and acetylene were used directly from cylinders, without further purification.

Infrared, mass, and n.m.r. spectra were obtained on Perkin-Elmer 257, A.E.I. MS 12, and Varian XL-100 spectrometers, respectively.

$[Os_3(CO)_{11}(NCCH_3)]$.—This compound was freshly prepared for each of the subsequent reactions. Typically, $[Os_3(CO)_{12}]$ (100 mg) was slurried in CH_2Cl_2 (60 cm³) and CH_3CN (1 cm³). Solid sublimed NMe_3O (9 mg) was added to the solution. When all the $[Os_3(CO)_{12}]$ had dissolved and the i.r. spectrum of the solution showed no remaining traces of it, the solution was filtered through a short silica gel column. This solution was either used directly or solid $[Os_3(CO)_{11}(NCCH_3)]$ was isolated by removing the solvent.

Reactions of $[Os_3(CO)_{11}(NCCH_3)]$.—*With acetylene.* This reaction was carried out by bubbling C_2H_2 through a CH_2Cl_2 solution of $[Os_3(CO)_{11}(NCCH_3)]$ for 2 h. When the CH_2Cl_2 was ‘ wet,’ work-up by preparative t.l.c. yielded three bands: a bright yellow band, consisting of $[Os_3(CO)_{10}$-

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† Nonacarbonyl-μ-hydrido-μ_3-[1—3-η-(1-hydroxyprop-1-enyl-3-ylidene)]-*triangulo*-triosmium and nonacarbonyl-μ-hydrido-μ_3-[1—3-η-(1-methoxyprop-1-enyl-3-ylidene)]-*triangulo*-triosmium, respectively.

(C_2H_2)] (mass spectrum, *m/e* 882 [$P - 10$ CO]$^+$) in 8% yield; a pale yellow slow-moving band yielding *ca.* 70% [$Os_3(CO)_9$-(C_3H_3O)H]; and a red band best eluted with neat CH_2Cl_2 and consisting of [$Os_3(CO)_{10}(C_2H_2)_2$] (mass spectrum, *m/e* 908 [$P - 9$ CO]$^+$) in 6% yield.

With RCCH. For R = CH_3 the reaction was carried out as for acetylene. For R = Ph, PhCCH (0.5 cm^3) was added to a solution of [$Os_3(CO)_{11}(NCCH_3)$] in CH_2Cl_2. The solution was allowed to stand overnight before work-up by preparative t.l.c. The second pale yellow band yielded 50% [$Os_3(CO)_9(PhC_3HOH)H$].

Methyl Ether Derivatives.—The compound [$Os_3(CO)_9$-(RC_3HOH)H] was dissolved in a minimum of tetrahydrofuran (thf). Excess of NaH, washed with hexane, was added. When effervescence had ceased a large excess of MeI was added and the solution warmed to 45 °C for 1 h. Preparative t.l.c. yielded only one product, [$Os_3(CO)_9$-(RC_3HOCH_3)], in high yield.

X-*Ray Structural Analysis of* [$Os_3(CO)_9(C_3H_2OH)H$] (7).—Pale yellow rectangular blocks of (7) were obtained by slow evaporation from octane. Several suitable crystals were mounted on the ends of glass fibres. 1 936 Intensities were measured on a Stoe AED four-circle diffractometer, using Mo-K_α radiation and a crystal of dimensions *ca.* 0.100 × 0.231 × 0.190 mm. Cell constants were derived from angular measurements of 20 strong reflections ($15 < 2\theta < 25°$). Data were collected in the range $3.0 \leqslant 2\theta \leqslant 45°$ using a 140-step ω—θ scan procedure; the step scan angle was fixed at 0.01° with a counting time of 0.5 s per step. Stationary backgrounds were recorded for 17.5 s at each end of the scan range. Reflections with intensities of $\leqslant 5$ counts s^{-1} from a 1-s pre-scan were not measured. Two check reflections were monitored every 50 measurements throughout data collection and showed no significant variation.

Lorentz polarization and numerical absorption corrections were applied. The crystal was bounded by the planes (010), (0$\bar{1}$0), (101), ($\bar{1}$0$\bar{1}$), (10$\bar{1}$), and ($\bar{1}$01), and transmission factors ranged from 0.040 to 0.129. Equivalent reflections were averaged to give 1 327 unique observed intensities [$F > 3\sigma(F)$].

Crystal data. $C_{12}H_4O_{10}Os_3$, *M* = 878.75, Orthorhombic, *a* = 16.291(5), *b* = 16.861(5), *c* = 12.234(3) Å, *U* = 3 360.5 Å^3, D_c = 3.47 g cm^{-3}, *Z* = 8, D_m not measured, *F*(000) = 3 070.83, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 226.74 cm^{-1}, space group *Pbca* from systematic absences.

The three Os atom positions were located by multisolution Σ_2 sign expansion, and all the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. The oxygen of the allyl alcohol was found to be positionally disordered between sites bonding to C(1) or C(3). During refinement the occupancies were set at *k* and 1 − *k* for the two oxygen atoms and assigned a common isotropic temperature factor; *k* refined to 0.512(33). The structure was refined by full-matrix least squares. The Os atoms were assigned anisotropic thermal parameters and the C and O atoms individual isotropic temperature factors. Refinement continued until the shift/e.s.d. (estimated standard deviation) for all parameters was reduced to <0.004; in the last cycles a weighting scheme of the form $w = 1.345\,4/[\sigma^2(F) + 0.001\,5(F)^2]$ was introduced. A difference synthesis calculated at this stage revealed ripples around the metal atoms but not the positions of the hydrogen atoms. The converged residuals were *R* 0.060 and *R'* 0.060 [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}(F_o)$].

X-*Ray Structural Analysis of* [$Os_3(CO)_9(C_3H_2OCH_3)H$] (8).—Yellow block-shaped crystals of (8) were deposited by slow evaporation from acetonitrile. Suitable crystals were mounted on glass fibres, and 2 146 reflections ($3.0 < 2\theta \leqslant 55.0°$) recorded on a crystal with dimensions *ca.* 0.169 × 0.113 × 0.075 mm using a similar mode to that described for [$Os_3(CO)_9(C_3H_2OH)H$]. The check reflections showed no significant variation in intensity.

A semiempirical absorption correction based on a pseudo-ellipsoid model and 295 azimuthal scan data from eight independent reflections was applied. Transmission factors ranged from 0.365 to 0.536 for the full data. Lorentz polarization corrections were also applied, and equivalent reflections averaged to give 1 671 unique observed intensities [$F > 4\sigma(F)$].

TABLE 1

Atom co-ordinates (× 10^4)

Atom	*x/a*	*y/b*	*z/c*
(*a*) Compound (7)			
Os(1)	3 639(1)	−75(1)	2 379(1)
Os(2)	3 366(1)	1 607(1)	1 780(1)
Os(3)	4 776(1)	1 121(1)	2 914(1)
C(11)	4 123(27)	−815(27)	3 325(42)
O(11)	4 473(20)	−1 287(18)	3 846(28)
C(12)	3 196(20)	−879(18)	1 507(31)
O(12)	2 991(19)	−1 324(16)	798(27)
C(13)	2 701(24)	−56(21)	3 328(36)
O(13)	2 155(20)	−63(16)	3 924(29)
C(21)	2 752(32)	1 798(28)	533(48)
O(21)	2 441(25)	1 898(23)	−300(37)
C(22)	3 551(27)	2 660(27)	2 047(40)
O(22)	3 699(20)	3 343(19)	2 317(29)
C(23)	2 453(24)	1 628(20)	2 732(31)
O(23)	1 888(18)	1 710(16)	3 292(25)
C(31)	5 636(23)	568(21)	3 550(34)
O(31)	6 202(19)	232(17)	3 993(27)
C(32)	5 321(22)	2 062(20)	3 121(32)
O(32)	5 669(20)	2 671(19)	3 251(29)
C(33)	4 095(23)	1 251(22)	4 145(35)
O(33)	3 708(18)	1 393(16)	4 894(27)
C(1)	4 589(24)	1 465(21)	1 125(36)
C(2)	4 992(22)	850(19)	1 133(32)
C(3)	4 733(21)	120(18)	1 660(30)
O(4)	5 304(29)	−416(27)	1 450(42)
O(5)	4 927(31)	2 078(29)	489(43)
(*b*) Compound (8)			
Os(1)	1 789(2)	758(1)	2 911(2)
Os(2)	4 193(2)	1 442(1)	2 396(2)
Os(3)	549(2)	1 302(1)	−58(2)
C(1)	2 188(41)	1 361(8)	3 969(41)
C(2)	1 774(41)	1 796(10)	3 226(35)
C(3)	976(50)	1 797(50)	1 563(40)
O(1)	602(36)	2 231(7)	857(28)
C(4)	1 124(75)	2 608(10)	1 859(57)
C(11)	3 677(64)	525(13)	4 769(55)
O(11)	4 954(42)	443(9)	5 914(35)
C(12)	−346(51)	513(10)	3 554(41)
O(12)	−1 549(43)	368(9)	4 009(34)
C(13)	2 155(50)	255(11)	1 622(41)
O(13)	2 387(37)	−47(8)	862(31)
C(21)	5 093(46)	988(10)	1 220(38)
O(21)	5 637(34)	713(7)	644(28)
C(22)	6 450(55)	1 421(11)	4 235(44)
O(22)	7 923(45)	1 397(8)	5 326(36)
C(23)	5 300(52)	1 887(11)	1 499(42)
O(23)	5 791(40)	2 200(9)	881(33)
C(31)	1 212(48)	1 671(11)	−1 549(40)
O(31)	1 714(36)	1 921(8)	−2 357(29)
C(32)	−2 263(46)	1 365(9)	−1 203(35)
O(32)	−3 887(41)	1 402(8)	−1 733(33)
C(33)	961(49)	820(11)	−1 370(49)
O(33)	1 059(37)	540(8)	−2 917(31)

Crystal data. $C_{13}H_6O_{10}Os_3$, *M* = 892.78, Monoclinic,

$a = 6.975(3)$, $b = 30.960(6)$, $c = 8.695(4)$ Å, $\beta = 107.62(2)°$, $U = 1\ 789.6$ Å^3, $D_c = 3.31$ g cm^{-3}, $Z = 4$, D_m not measured, $F(000) = 1\ 567.41$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) $= 212.90$ cm^{-1}, space group $P2_1/n$ from systematic absences.

The Os atoms were located by multisolution Σ_2 sign expansion, and the non-hydrogen atoms from a subsequent electron-difference synthesis. The structure was refined by full-matrix least squares with the Os atoms, the C and O atoms of the organic ligand assigned anisotropic thermal parameters, and the carbonyl C and O atoms isotropic temperature factors. The hydrogen atoms were not located. With weights $w = 0.809\ 4/[\sigma^2(F) + 0.001\ |F|^2]$, Δw^2 was fairly independent of sin θ and $|F_o|$. The converged residuals were R 0.053 and R' 0.053 ($=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$). A final difference synthesis revealed no regions of significant electron density.

TABLE 2

Selected spectroscopic data for $[Os_3(CO)_9(RC_3HOR')H]$

		Infrared (cm^{-1})	N.m.r. [a]	Mass [b]
(7)	$[Os_3(CO)_9(C_3H_2OH)H]$	3 609w, 3 510w, 2 099m, 2 072 (sh), 2 069s, 2 048vs, 2 020s, 2 010w, 2 007w, 2 001m, 1 998m, 1 988w, 1 983w	8.58 (dd) (1), 7.92 (dd) (1), −19.18 (dd) (1)	884
(11)	$[Os_3(CO)_9(PhC_3HOH)H]$	3 608w, 3 512m, 2 097m, 2 072 (sh), 2 068s, 2 047vs, 2 019s, 2 010w, 2 005w, 2 001m, 1 997m, 1 988w, 1 982w	8 42 (d) (1), 7.49 (m) (5), −18.55 (d) (1)	960
(9)	$[Os_3(CO)_9(H_3CC_3HOH)H]$	3 608w, 3 509w, 2 097m, 2 073 (sh), 2 069s, 2 048vs, 2 020s, 2 012w, 2 008w, 2 002m, 1 998m, 1 989w, 1 983w	8.39 (d) (1), 2.95 (s) (3), −19.01 (d) (1)	898
(8)	$[Os_3(CO)_9(C_3H_2OCH_3)H]$	2 098m, 2 071s, 2 044vs, 2 020s, 2 007w, 2 000m, 1 982w	8 65 (dd) (1), 8.00 (dd) (1), 3.78 (s) (3), −19.16 (dd) (1)	898
(10)	$[Os_3(CO)_9(PhC_3HOCH_3)H]$	2 097m, 2 071s, 2 042vs, 2 020s, 2 007w, 1 999m, 1 979w	8.50 (d) (1), 7.48 (m) (5), 3.75 (s) (3), −18.56 (d) (1)	974

[a] Proton chemical shifts in p.p.m. relative to $SiMe_4$. The chemical shifts for the O–H protons are not given since these depend on temperature and solvent (see text). [b] m/e Values for molecular ions (based on ^{192}Os) minus 9 CO.

Complex neutral-atom scattering factors [7] were employed in both structure refinements. Final atomic co-ordinates for (7) and (8) are given in Table 1, while details of thermal parameters, molecular planes, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22829 (22 pp.).* All computing was carried out on the IBM 376/165 computer at the University of Cambridge using the SHELX 76 program system.[8] Figures 1 and 2 were drawn with the PLUTO program written by Dr. W. D. S. Motherwell.

RESULTS AND DISCUSSION

Spectroscopic data for the allyl compounds are given in Table 2. Bond lengths and angles from the X-ray analysis for (7) are presented in Table 3 and those for (8) in Table 4. Figure 1 is the molecular geometry of (7) and shows only one orientation of the disordered allyl alcohol, while the structure of (8) is shown in Figure 2. For both structures, the trinuclear molecules are separated by normal van der Waals distances and there are no short intermolecular contacts.

Formation of (7), (9), *and* (11).—Reaction of acetylene with $[Os_3(CO)_{11}(NCCH_3)]$ in the presence of water yields three products. Two of these are formed in less than 8% yield and are of known stoicheiometry, $[Os_3(CO)_{10}(C_2H_2)]$ (12) and $[Os_3(CO)_9(C_4H_4CO)]$ (13). The major product, $[Os_3(CO)_9(C_3H_2OH)H]$ (7), is formed in 50—70% yield, apparently from an acetylene molecule and a co-ordinated carbonyl group. Additional protons are incorporated from water.

Interestingly, two of the products, (7) and (13), incorporate CO into the organic ligand. Even under the mild conditions of the reaction carbon monoxide is eliminated to allow the acetylene to be a net donor of more than two electrons.

When the alkyne is MeCCH or PhCCH compounds (9) and (11), respectively, are formed in high yield. The production of the allyl alcohol molecules occurs only for terminal alkynes. For example, when diphenylacetylene was allowed to react with $[Os_3(CO)_{11}(NCCH_3)]$ in the presence of water for 96 h at 20 °C, 60% of this complex was recovered unchanged. The only product was $[Os_3(CO)_{10}(C_2Ph_2)]$.

The molecules (7), (9), and (11) exist as slowly interconverting isomers. The evidence for this is as follows.

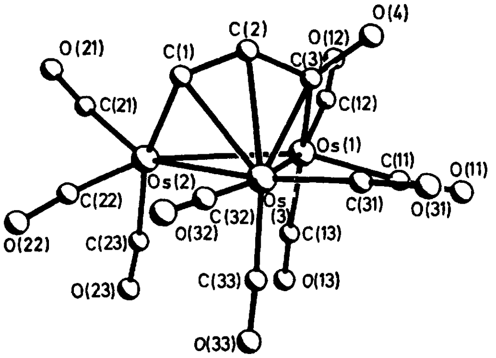

FIGURE 1 Molecular structure of $[Os_3(CO)_9(C_3H_2OH)H]$ including the atom-numbering scheme. Only one orientation of the disordered OH group has been shown for clarity

In the carbonyl-stretching region of the i.r. spectra for these molecules there are 11 absorptions. This is too many for compounds with only nine carbonyl ligands. Also, for each of these molecules there are two weak, but sharp, O–H stretches at 3 608 and 3 512 cm^{-1}.

The n.m.r. spectra for (7), (9), and (11) are straightforward in the allyl and hydride regions. There is no

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

evidence that the isomers give rise to separate sets of signals for these protons. The assignment of the O–H proton is less clear. For extremely dry samples at room temperature two broad resonances are observed, *e.g.* at 6.68 and 1.58 p.p.m. for (7) in CD_2Cl_2. Spin-saturation transfer [9] shows that these two resonances are due to exchanging protons. The total integration for these two signals corresponds to one proton. In slightly wet samples a single broad resonance is observed (the chemical shift varies with the amount of water present). Upon cooling this resonance collapses and two new resonances appear at approximately the positions observed for the anhydrous sample.

TABLE 3

Bond lengths (Å) and angles (°) for compound (7)

Os(2)–Os(1)	2.962(3)	C(11)–Os(1)	1.875(48)
Os(3)–Os(1)	2.815(3)	C(12)–Os(1)	1.870(34)
Os(3)–Os(2)	2.806(3)	C(13)–Os(1)	1.919(42)
C(3)–Os(1)	2.015(34)	C(21)–Os(2)	1.852(58)
C(1)–Os(2)	2.161(40)	C(22)–Os(2)	1.831(46)
C(1)–Os(3)	2.285(43)	C(23)–Os(2)	1.889(39)
C(2)–Os(3)	2.254(39)	C(31)–Os(3)	1.854(39)
C(3)–Os(3)	2.281(34)	C(32)–Os(3)	1.837(34)
C(2)–C(1)	1.228(48)	C(33)–Os(3)	1.882(43)
C(3)–C(2)	1.451(47)	O(11)–C(11)	1.168(48)
O(4)–C(3)	1.323(56)	O(12)–C(12)	1.194(10)
O(5)–C(1)	1.405(62)	O(13)–C(13)	1.150(43)
O(31)–C(31)	1.210(45)	O(21)–C(21)	1.151(58)
O(32)–C(32)	1.183(41)	O(22)–C(22)	1.221(49)
O(33)–C(33)	1.138(44)	O(23)–C(23)	1.156(41)
Os(3)–Os(1)–Os(2)	58.0(1)	C(11)–Os(1)–Os(2)	148.5(14)
Os(3)–Os(2)–Os(1)	58.3(1)	C(11)–Os(1)–Os(3)	93.2(14)
Os(2)–Os(3)–Os(1)	63.6(1)	C(12)–Os(1)–Os(2)	119.7(10)
C(3)–Os(1)–Os(2)	82.4(9)	C(12)–Os(1)–Os(3)	154.9(11)
C(3)–Os(1)–Os(3)	53.3(10)	C(13)–Os(1)–Os(2)	90.8(10)
C(1)–Os(2)–Os(1)	81.3(10)	C(13)–Os(1)–Os(3)	111.8(11)
C(1)–Os(2)–Os(3)	52.9(11)	C(21)–Os(2)–Os(1)	116.8(15)
C(1)–Os(3)–Os(1)	82.7(9)	C(21)–Os(2)–Os(3)	154.2(16)
C(1)–Os(3)–Os(2)	48.9(10)	C(22)–Os(2)–Os(1)	149.3(15)
C(2)–Os(3)–Os(1)	74.5(9)	C(22)–Os(2)–Os(3)	93.5(14)
C(2)–Os(3)–Os(2)	73.1(9)	C(23)–Os(2)–Os(1)	89.1(10)
C(3)–Os(3)–Os(1)	45.1(9)	C(23)–Os(2)–Os(3)	110.2(11)
C(3)–Os(3)–Os(2)	81.8(8)	C(31)–Os(3)–Os(1)	103.6(11)
C(12)–Os(1)–C(11)	91.8(17)	C(31)–Os(3)–Os(2)	166.7(11)
C(13)–Os(1)–C(11)	88.5(18)	C(32)–Os(3)–Os(1)	165.8(11)
C(13)–Os(1)–C(12)	92.9(16)	C(32)–Os(3)–Os(2)	102.2(11)
C(22)–Os(2)–C(21)	93.8(21)	C(33)–Os(3)–Os(1)	83.2(11)
C(23)–Os(2)–C(21)	94.6(20)	C(33)–Os(3)–Os(2)	83.1(12)
C(23)–Os(2)–C(22)	90.1(18)	C(3)–Os(1)–C(11)	90.3(17)
C(32)–Os(3)–C(31)	90.6(16)	C(3)–Os(1)–C(12)	102.1(14)
C(33)–Os(3)–C(31)	99.7(17)	C(3)–Os(1)–C(13)	165.0(15)
C(33)–Os(3)–C(32)	94.2(16)	C(1)–Os(2)–C(21)	102.2(20)
C(2)–Os(3)–C(1)	31.4(12)	C(1)–Os(2)–C(22)	91.2(16)
C(3)–Os(3)–C(1)	62.6(13)	C(1)–Os(2)–C(23)	163.0(16)
C(3)–Os(3)–C(2)	37.3(12)	C(1)–Os(3)–C(31)	129.1(16)
Os(3)–C(1)–Os(2)	78.2(14)	C(1)–Os(3)–C(32)	88.6(15)
C(2)–C(1)–Os(2)	125.6(31)	C(1)–Os(3)–C(33)	131.2(15)
C(2)–C(1)–Os(3)	72.9(28)	C(2)–Os(3)–C(31)	100.7(15)
O(5)–C(1)–Os(2)	119.1(30)	C(2)–Os(3)–C(32)	103.5(15)
O(5)–C(1)–Os(3)	131.7(31)	C(2)–Os(3)–C(33)	152.7(15)
O(5)–C(1)–C(2)	114.6(42)	C(3)–Os(3)–C(31)	86.2(15)
C(1)–C(2)–Os(3)	75.7(29)	C(3)–Os(3)–C(32)	138.3(15)
C(3)–C(2)–Os(3)	72.4(21)	C(3)–Os(3)–C(33)	127.3(14)
C(3)–C(2)–C(1)	124.4(37)	O(11)–C(11)–Os(1)	174.3(41)
Os(3)–C(3)–Os(1)	81.6(12)	O(12)–C(12)–Os(1)	167.9(30)
C(2)–C(3)–Os(1)	126.2(24)	O(13)–C(13)–Os(1)	177.3(34)
C(2)–C(3)–Os(3)	70.3(20)	O(21)–C(21)–Os(2)	173.1(49)
O(4)–C(3)–Os(1)	126.5(30)	O(22)–C(22)–Os(2)	174.1(42)
O(4)–C(3)–Os(3)	127.9(31)	O(23)–C(23)–Os(2)	174.0(31)
O(4)–C(3)–C(2)	106.8(35)	O(31)–C(31)–Os(3)	177.5(34)
O(32)–C(32)–Os(3)	179.6(22)	O(33)–C(33)–Os(3)	174.3(34)

Thus, the two isomers exchange very slowly under anhydrous conditions while the presence of moisture apparently catalyses the exchange. Also the two isomers differ only in the nature of the O–H proton (i.r.) but are identical with respect to the remainder of the allyl ligand (n.m.r.). The extra absorptions in the carbonyl-stretching region of the i.r. spectrum implies that the two isomers interact differently with the $Os_3(CO)_9$ unit.

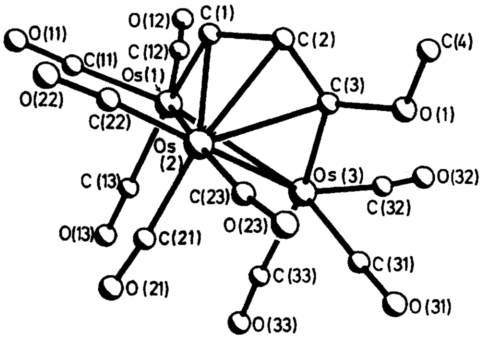
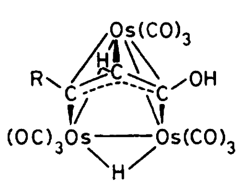
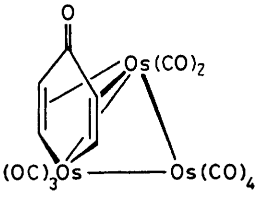


FIGURE 2 Molecular structure of $[Os_3(CO)_9(C_3H_2OCH_3)H]$ including the atom-numbering scheme

The Molecular Structure of $[Os_3(CO)_9(C_3H_2OH)H]$ (7).—The determination of the molecular structure of (7) (Figure 1) confirms that the organic ligand is an allyl alcohol but does not resolve the nature of the two isomers. The allyl group lies over the top of the Os_3 triangle and co-ordinates to the three metal atoms *via* two σ bonds and a π-allyl bond, *i.e.* as a five-electron donor. This type of bonding to a face of a trinuclear cluster is well established in many compounds.[10-13] The two metal–metal bonds to the unique Os(3) atom (average 2.810 Å) are similar to the value of 2.819(1) Å for the oxygen-bridged Os–Os edge in $[Os_3(CO)_8\{C(O)C(CHMe)CHCHCEt\}H]$.[14] The third edge of the triangle is extended in length to a value which is indicative [15] of the bond being hydride bridged. This is confirmed by an analysis of the distribution of the carbonyl ligands *cis* to this edge which shows that they bend away with an average Os–Os–C(carbonyl) angle of 118°. This may be compared to an average *cis* Os–Os–C angle of 96° for the other edges.



R
(7) H
(9) Me
(11) Ph



(13)

The OH group of the allyl alcohol is positionally disordered in a *ca.* 1 : 1 ratio. This renders the carbon atoms C(1) and C(3) indistinguishable due to an interchange of sites in the disorder, and the hydroxyl hydrogen can also orient itself in two chemically indistinguishable ways. This disorder, in the crystal, does not explain the two isomers in solution since the two arrangements of the C_3H_2OH ligand are simply mirror images of each other and necessarily have identical spectral properties. Both isomers are apparently present in the crystal since a crystalline sample of (7) dissolved in dry cyclohexane to give a typical i.r. spectrum.

TABLE 4

Bond lengths (Å) and angles (°) for compound (8)

Os(2)–Os(1)	2.819(3)	C(11)–Os(1)	1.892(46)
Os(3)–Os(1)	2.892(3)	C(12)–Os(1)	1.901(35)
Os(3)–Os(2)	2.814(3)	C(13)–Os(1)	1.982(34)
C(1)–Os(1)	2.062(28)	C(21)–Os(2)	1.950(32)
C(1)–Os(2)	2.246(30)	C(22)–Os(2)	1.875(37)
C(2)–Os(2)	2.304(28)	C(23)–Os(2)	1.862(35)
C(3)–Os(2)	2.405(33)	C(31)–Os(3)	1.888(34)
C(3)–Os(3)	2.043(31)	C(32)–Os(3)	1.922(31)
C(2)–C(1)	1.484(35)	C(33)–Os(3)	1.952(34)
C(3)–C(2)	1.383(40)	O(11)–C(11)	1.146(45)
O(1)–C(3)	1.465(37)	O(12)–C(12)	1.124(36)
C(4)–O(1)	1.436(38)	O(13)–C(13)	1.183(37)
O(21)–C(21)	1.113(33)	O(31)–C(31)	1.167(36)
O(22)–C(22)	1.171(40)	O(32)–C(32)	1.092(34)
O(23)–C(23)	1.208(38)	O(33)–C(33)	1.143(36)

Os(3)–Os(1)–Os(2)	58.0(1)	C(11)–Os(1)–Os(2)	97.4(13)
Os(3)–Os(2)–Os(1)	63.9(1)	C(11)–Os(1)–Os(3)	154.1(13)
Os(2)–Os(3)–Os(1)	58.1(1)	C(12)–Os(1)–Os(2)	154.7(10)
C(1)–Os(1)–Os(2)	52.0(8)	C(12)–Os(1)–Os(3)	115.7(10)
C(1)–Os(1)–Os(3)	80.8(9)	C(13)–Os(1)–Os(2)	108.5(10)
C(1)–Os(2)–Os(1)	46.4(7)	C(13)–Os(1)–Os(3)	90.5(10)
C(1)–Os(2)–Os(3)	81.9(8)	C(21)–Os(2)–Os(1)	81.0(9)
C(2)–Os(2)–Os(1)	77.3(7)	C(21)–Os(2)–Os(3)	81.5(9)
C(2)–Os(2)–Os(3)	74.5(8)	C(22)–Os(2)–Os(1)	103.0(11)
C(3)–Os(2)–Os(1)	81.1(8)	C(22)–Os(2)–Os(3)	166.9(11)
C(3)–Os(2)–Os(3)	45.3(8)	C(23)–Os(2)–Os(1)	164.6(11)
C(3)–Os(3)–Os(1)	83.3(10)	C(23)–Os(2)–Os(3)	101.0(11)
C(3)–Os(3)–Os(2)	56.7(10)	C(31)–Os(3)–Os(1)	150.3(10)
C(2)–Os(2)–C(1)	38.0(9)	C(31)–Os(3)–Os(2)	94.3(10)
C(3)–Os(2)–C(1)	62.5(10)	C(32)–Os(3)–Os(1)	119.3(8)
C(3)–Os(2)–C(2)	34.1(9)	C(32)–Os(3)–Os(2)	157.4(8)
C(12)–Os(1)–C(11)	90.0(16)	C(33)–Os(3)–Os(1)	91.1(10)
C(13)–Os(1)–C(11)	90.4(16)	C(33)–Os(3)–Os(2)	107.6(10)
C(13)–Os(1)–C(12)	95.6(14)	C(11)–Os(1)–C(1)	90.0(15)
C(22)–Os(2)–C(21)	95.8(14)	C(12)–Os(1)–C(1)	104.1(13)
C(23)–Os(2)–C(21)	94.2(14)	C(13)–Os(1)–C(1)	160.3(12)
C(23)–Os(2)–C(22)	92.0(15)	C(21)–Os(2)–C(1)	126.7(11)
C(32)–Os(3)–C(31)	90.4(13)	C(21)–Os(2)–C(2)	152.9(12)
C(33)–Os(3)–C(31)	87.2(14)	C(21)–Os(2)–C(3)	126.2(12)
C(33)–Os(3)–C(32)	94.8(13)	C(22)–Os(2)–C(1)	89.6(14)
O(11)–C(11)–Os(1)	169.8(37)	C(22)–Os(2)–C(2)	104.7(13)
O(12)–C(12)–Os(1)	176.6(32)	C(22)–Os(2)–C(3)	137.6(13)
O(13)–C(13)–Os(1)	179.5(27)	C(23)–Os(2)–C(1)	138.7(12)
O(21)–C(21)–Os(2)	175.2(29)	C(23)–Os(2)–C(2)	102.4(13)
O(22)–C(22)–Os(2)	175.9(33)	C(23)–Os(2)–C(3)	90.2(13)
O(23)–C(23)–Os(2)	171.9(31)	C(31)–Os(3)–C(3)	90.3(14)
O(31)–C(31)–Os(3)	174.1(30)	C(32)–Os(3)–C(3)	101.2(12)
O(31)–C(32)–Os(3)	174.1(29)	C(33)–Os(3)–C(3)	163.9(13)
O(33)–C(33)–Os(3)	175.1(30)	Os(2)–C(1)–Os(1)	81.6(11)
C(1)–C(2)–Os(2)	68.9(16)	C(2)–C(1)–Os(1)	130.2(23)
C(3)–C(2)–Os(2)	77.0(18)	C(2)–C(1)–Os(2)	73.1(16)
C(3)–C(2)–C(1)	114.9(28)	O(1)–C(3)–Os(2)	125.2(21)
Os(3)–C(3)–Os(2)	78.0(10)	O(1)–C(3)–Os(3)	115.3(21)
C(2)–C(3)–Os(2)	69.0(18)	O(1)–C(3)–C(2)	113.9(26)
C(2)–C(3)–Os(3)	130.4(25)	C(4)–O(1)–C(3)	120.6(28)

Preparation and Molecular Structure of $[Os_3(CO)_9(C_3H_2OCH_3)H]$ (8).—The methyl ethers of (7) and (9), (8) and (10) respectively, are easily prepared by reaction with sodium hydride and methyl iodide. The yields of these reactions are high, nearly 80%, which indicates that both isomers of (7) and (9) react to give the methyl ether derivatives.

The i.r. spectra of (8) and (10) are greatly simplified in comparison to their respective allyl alcohol precursors. Both have only seven absorptions in the carbonyl-stretching region. Furthermore, each of the seven observed bands corresponds to an absorption of the parent molecules. This indicates that the methyl ether derivatives exist in only one isomeric form which is identical in stereochemistry to one of the isomers of the parent allyl alcohol molecules.

Figure 2 shows the molecular structure of (8), and it is clear that the methyl group, C(4), is directed away from the $Os_3(CO)_9$ unit. The ether oxygen atom, O(1), is nearly close packed with respect to the nearest two carbonyl groups C(23) and C(31). The contacts are 3.33 and 2.85 Å, respectively. Rotation about the C(3)–O(1) bond in the ligand is expected to be restricted for steric reasons since the ' closest approach,' allowing for free rotation, between C(4) and O(31) is estimated to be less than 2.4 Å.

The dimensions of the Os_3 triangle are similar to those in the parent alcohol. The distribution of the carbonyl ligands again indicates that the hydride bridges the long Os(1)–Os(3) edge. The allyl ether co-ordinates to the metal triangle *via* σ bonds to Os(1) and Os(3) and a π-allyl bond to Os(2). The group is slightly tilted with the Os(2)–C(1) distance significantly shorter than Os(2)–C(3). The C(1)–C(2) and C(2)–C(3) distances reflect the electron delocalization in this planar system. The carbonyl ligands are all terminal but show slight deviation from linearity because of the steric influence of the organic group.

Conclusion.—The spectroscopic and crystallographic data lead to the following postulates regarding the two isomers of the allyl alcohol molecules (7), (9), and (11). One of the isomers has the same stereochemistry as observed in the methyl ether derivatives with a proton replacing the methyl group. This proton is directed away from the cluster. The second isomer arises because of restricted rotation about the alcoholic C–O bond, and an orientation with the proton pointing towards the cluster is of nearly equal energy to the orientation away from the cluster. This latter orientation is inaccessible for the methyl ether derivatives (8) and (10) in which the proton has been replaced by a more bulky methyl group.

The formation of molecules similar to (7), (9), and (11) is unprecedented under such mild conditions. Using the conditions described above alkynes will not function as simple two-electron donors on a triosmium cluster. Displacement of additional carbonyls and combination with co-ordinated CO, allowing the alkyne to donate three or four electrons, is apparently favoured over the donation of just two electrons.

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REFERENCES

[1] O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.

[2] R. P. Ferrani, G. A. Vaglio, O. Gambino, M. Valle, and G. Cetini, *J.C.S. Dalton*, 1972, 1998.

[3] G. A. Vaglio, O. Gambino, R. P. Ferrari, and G. Cetini, *Inorg. Chim. Acta*, 1973, **7**, 193.

[4] A. J. Deeming, S. Hasso, and M. Underhill, *J.C.S. Dalton*, 1975, 1614.

[5] M. Tachikawa and J. R. Shapley, *J. Organometallic Chem.*, 1977, **124**, C19.

[6] A. J. Carty, W. F. Smith, and N. J. Taylor, *J. Organometallic Chem.*, 1978, **146**, Cl.

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[8] SHELX 76, a program system for crystal-structure determination, G. M. Sheldrick, University of Cambridge, 1976.

[9] S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892; B. E. Mann, *J. Magn. Reson.*, 1976, **21**, 17.

[10] M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735.

[11] G. Gervasio, S. Aime, L. Milone, E. Sappa, and M. Franchini-Angela, *Transition Metal Chem.*, 1976, **1**, 96; G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, 1976, **15**, 1221; G. Gervasio, *J.C.S. Chem. Comm.*, 1976, 25.

[12] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 525.

[13] B. E. R. Schilling and R. Hoffman, *J. Amer. Chem. Soc.*, 1979, **101**, 3456.

[14] M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1978, **17**, 1291.

[15] M. R. Churchill, B. G. De Boer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.