Triosmium Clusters containing Ligands derived from Tropone (Cycloheptatrienone): Molecular Structure of an Oxidative Addition Product $[Os_3H(\mu_3\text{-}C_7H_5O)(CO)_9]$†

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Tropone (cycloheptatrienone, C_7H_6O) reacts in refluxing cyclohexane with $[Os_3H_2(CO)_{10}]$ to give the oxidative addition product $[Os_3H(C_7H_5O)(CO)_{10}]$ (**1**), also formed from $[Os_3(CO)_{10}(MeCN)_2]$, and the insertion product $[Os_3H(C_7H_7O)(CO)_{10}]$ (**2**). Structures based on spectroscopy are discussed. Compound (**1**) decarbonylates to $[Os_3H(C_7H_5O)(CO)_9]$ (**3**), the *X*-ray structure of which shows that the μ_3-troponyl ligand is involved in a μ-η^2-vinyl type bridge between two Os atoms and a donation through the oxygen atom of the ketonic group to the third Os atom. Hydrogenation of cluster (**1**) and decarbonylation of cluster (**2**) lead to the derivatives $[Os_3H_2(C_7H_6O)(CO)_9]$ (**4**) and $[Os_3(C_7H_8O)(CO)_9]$ (**5**). Cluster (**4**) is directly related to the reported structures $[Os_3H_2(C_6H_4O)(CO)_9]$ from phenol and $[Os_3H_2(C_6H_8O)(CO)_9]$ from cyclohexanone. All five products from tropone contain Os–O bonds and the chemistry is quite unlike any known tropone–transition metal chemistry.

Previous work on the organometallic chemistry of tropone (cycloheptatrienone, C_7H_6O)[1] has shown that the ligand can form π complexes such as $[Fe(\eta^4\text{-}C_7H_6O)(CO)_3]$[2] and $[Cr(\eta^6\text{-}C_7H_6O)(CO)_3]$.[3] To our knowledge no evidence for co-ordination through the ketonic group has been found for simple mononuclear compounds. Based on earlier work, two differences in triosmium chemistry might be expected: oxidative addition with C–H cleavage to give σ-bonded complexes and co-ordination through the ketonic oxygen atom. Both features have been established for various saturated and unsaturated ketones[4,5] and aldehydes.[6] In an extreme case we have shown that phenol can be trapped in a non-aromatic cyclohexa-2,4-dienone form in $[Os_3H_2(\mu_3\text{-}C_6H_4O)(CO)_9]$ which contains two Os–C σ bonds and ketone co-ordination.[7,8] In this paper we will show that both features dominate the chemistry of tropone with Os_3 clusters and present the *X*-ray structure of the oxidative addition product $[Os_3H(\mu_3\text{-}C_7H_5O)(CO)_9]$ which confirms the presence of Os–C σ bonds and co-ordination through oxygen.

Results and Discussion

Reactions of Tropone with $[Os_3(CO)_{10}(MeCN)_2]$ *and with* $[Os_3H_2(CO)_{10}]$.—The starting materials were chosen because the former favours oxidative addition and the latter insertion into Os–H bonds. Reactions with tropone give fairly low yields of products but we have been able to establish the chemistry of compounds (1)—(5) as shown in Scheme 1. The bis-acetonitrile compound reacts with an excess of tropone in refluxing chloroform to give the oxidative addition compound $[Os_3H(C_7H_5O)(CO)_{10}]$ (1) (23%) but no other product could be isolated. I.r. and n.m.r. data (Table 1) agree with the structure shown in Scheme 1, in particular there are close analogies with $[Os_3H(C_6H_6O)(CO)_{10}]$, the oxidative addition product of cyclohex-2-enone, both in the i.r. and ^1H n.m.r. spectra.[4] The co-ordination of the ketonic group is confirmed by the lack of any ν(CO) (ketone) absorption above 1 610 cm^{-1}.

Thus tropone has donated the four electrons needed by the $Os_3(CO)_{10}$ group by oxidative addition with C–H bond cleavage and ketone co-ordination rather than by π donation from the unsaturated carbon system. This is quite unique for tropone in transition metal compounds but not unexpected from the known chemistry of unsaturated ketones with triosmium clusters.

Tropone also reacts with $[Os_3H_2(CO)_{10}]$ to give compound (1) (10%) as well as the insertion product $[Os_3H(C_7H_7O)(CO)_{10}]$ (2) (16%). The ^1H n.m.r. spectrum of (2) confirms that a H atom has transferred from osmium to the carbon atom of the tropone CO group. Seven ^1H n.m.r. signals and the observed couplings are consistent with the ring system shown for (2) in Scheme 1. The mode of attachment of the C_7H_7O ligand is not confirmed but is based on analogies with known compounds. The ν(CO) spectrum (Table 1) is consistent with the 4,4,2 distribution of CO ligands by comparison with related compounds with known structure of this type: $[Os_3(CO)_{10}(CH_2{=}CHOCOMe)]$[9] and $[Os_3H(MeC{=}CCOMe)(CO)_{10}]$.[4] The oxygen atom is sited axially and there are equatorial Os–C bonds in each of these compounds so we have illustrated compound (2) in this way.

Decarbonylation of Decacarbonyl Clusters.—Three nonacarbonyl clusters, (3)—(5), are formed by thermal or photochemical decarbonylation or hydrogenation of compounds (1) and (2) as shown in Scheme 1. We attempted to obtain these compounds directly but the direct reaction of $[Os_3(CO)_{12}]$ with tropone gave no reaction in refluxing heptane and >90% decomposition in refluxing nonane. However, the direct reaction of $[Os_3H_2(CO)_{10}]$ with tropone in refluxing nonane gave cluster (4) (20%) and this is the best route to this compound.

Compound (3), formed in 67% yield by decarbonylation of (1) at above 120 °C, is the most thoroughly studied product. This is derived simply by loss of CO from the $Os(CO)_4$ group of (1) with η^2 co-ordination of the troponyl ligand at this metal atom. The doubly bridging three-electron donor C_7H_5O in (1) becomes triply bridging and a five-electron donor in (3). This was largely apparent from the spectroscopic and analytical data (Table 1 and Experimental section), but the details of the attachment of the C_7H_5O ligand were established by a single-

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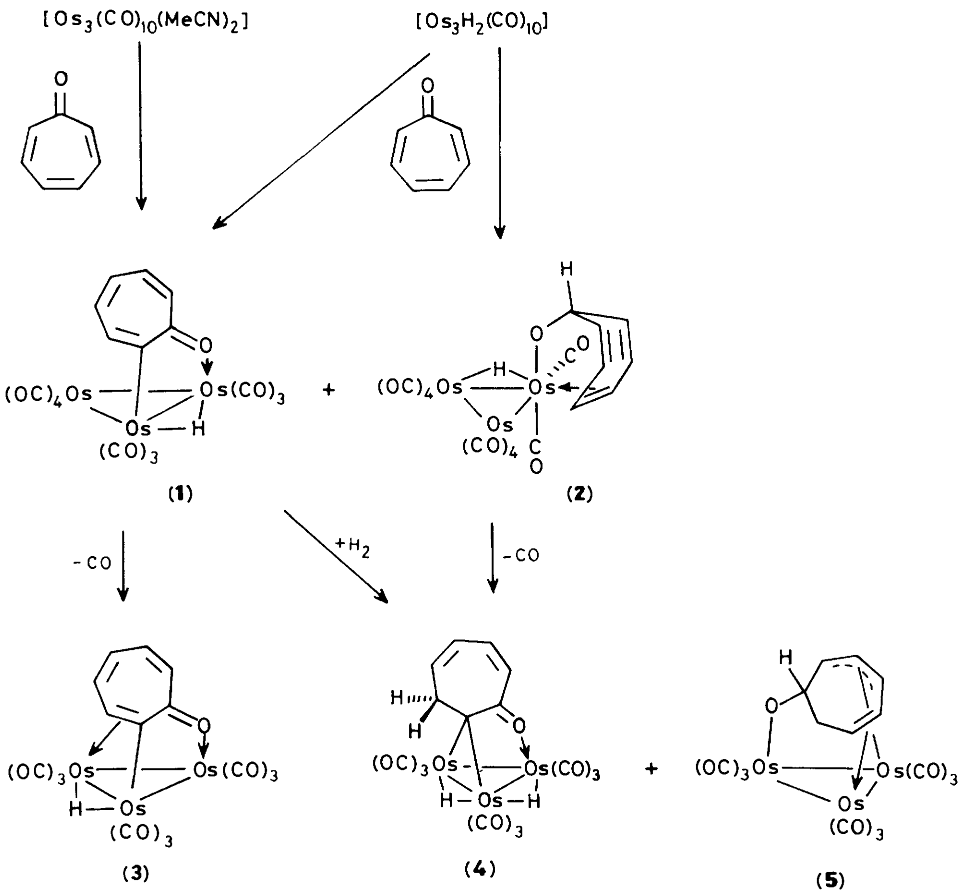
† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-hydrido-μ_3-[σ,η^2-2-oxocycloheptatrien-1-yl-$C^1(Os^{1,2})C^7(Os^1)O(Os^3)$]-*triangulo*-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 1.

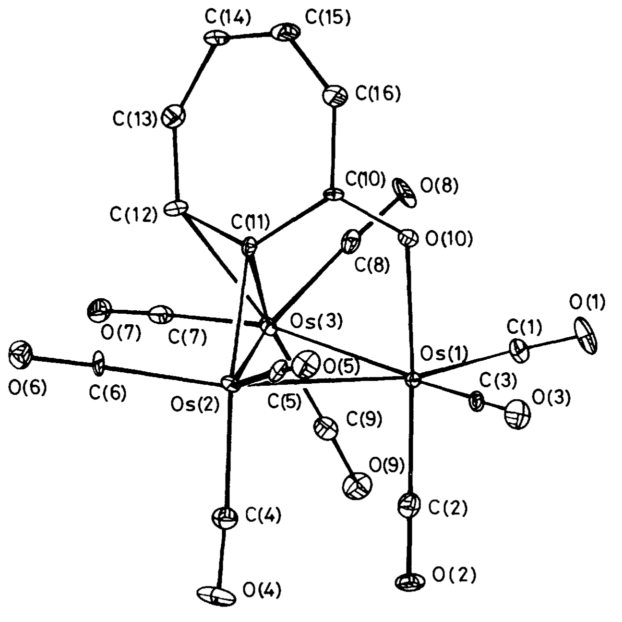
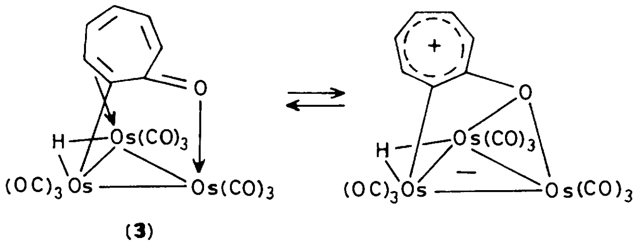


Figure. The molecular structure of (**3**). Thermal ellipsoids are drawn at the 10% probability level

crystal X-ray structure determination. Atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 3. The Figure shows the molecular structure of compound (**3**).

The geometry of the Os(2)Os(3)C(11)C(12) group of atoms in (**3**) might be compared with those known for the compounds $[\mathrm{Os_3H}(\mu\text{-}\eta^2\text{-vinyl})(\mathrm{CO})_{10}]$ where the vinyl group is CH=CH$_2$,[10] CH=CHEt,[11] CH=CHBu^t,[12] or PhC=CHPh.[13] The Os–C distances in this group support a μ-η^2-vinyl description for (**3**). For example, the Os(2)–C(11), Os(3)–C(11), and Os(3)–C(12) bonds [2.117(15), 2.239(13), and 2.381(14) Å respectively] might be compared with corresponding distances of 2.107(3), 2.273(3), and 2.362(3) Å in the simple CH=CH$_2$ compound.[10] The η^2 interaction is unsymmetrical to the same extent and the particularly long Os–C distance of 2.381(14) Å is characteristic of this ligand arrangement. The C–C distances within the tropone ligand are as expected for the alternation of single and double bonds and the C(10)–O(10) distance of 1.239(16) Å agrees with the ketonic description. The average Os–C (carbonyl) distance is 1.903(27) Å but it is noticeable that the shortest of these is Os(1)–C(2) [1.867(18) Å], indicating the weakness of the ketone to osmium bond and the strong π bonding to the ligand C(2)O(2) *trans* to it.



Scheme 2.

We looked for distortions in compound (**3**) towards an alternative zwitterionic tropylium-type form shown in Scheme 2

Table 1. I.r. and ^{1}H n.m.r. data for compounds (**1**)—(**5**)

Compound	ν(CO)^a/cm^{-1}	Organic ν(CO) or ν(C=C)/cm^{-1}	^{1}H N.m.r.^{b} δ	Assignment	J/Hz
[$Os_3H(C_7H_5O)(CO)_{10}$] (**1**)	2 102m, 2 062s, 2 050s, 2 019s, 2 006s, 1 990m, 1 985 (sh), 1 972w	1 611^c	8.92 (d)	H^3	9.1
		1 563^c	7.11 (m)	H^{4}H^5	
			6.99 (m)	H^{6}H^7	
			−12.32 (s)	OsH	
[$Os_3H(C_7H_7O)(CO)_{10}$] (**2**)	2 100m, 2 056s, 2 023vs, 2 019vs, 2 015 (sh), 1 991w, 1 987m, 1 978m, 1 956m	1 607^d	6.46 (dd)	H^1—H^7	9.7, 8.9
			6.23 (dd)		10.0, 6.8
			5.98 (t)^e		*ca.* 8.2
			5.81 (t)^e		*ca.* 8.2
			5.57 (t)^e		*ca.* 8.0
			4.96 (t)^e		*ca.* 8.0
			4.74 (t)		6.8
			−12.49 (s)	OsH	
[$Os_3H(C_7H_5O)(CO)_9$] (**3**)	2 085m, 2 053s, 2 036vs, 2 009m, 2 001s, 1 994m, 1 981w, 1 968m	1 624^d	4.28 (d)	H^7	5.3
		1 554^d	5.85 (d)	H^3	11.8
		1 516^d	6.29 (dd)	H^4	11.8, 7.7
			6.80 (dd)	H^6	11.5, 5.3
			7.28 (dd)	H^5	11.5, 7.7
			−16.60 (s)	OsH	
[$Os_3H_2(C_7H_6O)(CO)_9$] (**4**)	2 106m, 2 080vs, 2 052vs, 2 029s, 2 023vs, 2 010s, 1 999s, 1980m		6.26 (dd)	H^5	7.7, 4.6
			6.15 (d)	H^3	10.7
			5.54 (dd)	H^4	10.7, 4.6
			5.35 (dt)	H^6	7.7, 3.6
			2.67 (dd)^f	H^7	3.6, 10.2
			2.58 (dd)^f	H^7	3.6, 10.2
			−12.07 (d)	OsH	1.8
			−14.17 (d)	OsH	1.8
[$Os_3H_2(C_6H_8O)(CO)_9$]^g (**7**)	2 105w, 2 080s, 2 051s, 2 023s, 2 020 (sh), 2 010m, 1 998s, 1 970m	1 496	2.30 (m)	CH_2	
			1.3—1.9 (m)	$(CH_2)_3$	
			−12.36 (d)	OsH	
			−14.03 (d)	OsH	
[$Os_3(C_7H_8O)(CO)_9$] (**5**)	2 091w, 2 020m, 2 010s, 2 003m, 1 953w, 1 944w		5.83 (m)	H^1	$J_{1,2}$ 8.0
			5.30 (ddd)	H^5	$J_{2,3}$ 8.0
			5.04 (t)	H^2	$J_{3,4}$ 7.6
			4.97 (t)	H^4	$J_{4,5}$ 7.4
			4.48 (dd)	H^6	$J_{5,6}$ 5.9
			3.79 (dddd)	H^3	$J_{6,7a}$ 7.2
			1.35 (d)	H^{7a}	$J_{1,7a}$ 5.4
			0.87 (ddd)	H^{7b}	$J_{7a,7b}$ 15.5

[a] In cyclohexane. [b] Recorded at 20 °C in $CDCl_3$ at 200 MHz. [c] CH_2Cl_2 solution. [d] In Nujol. [e] Almost resolved into (dd). [f] Two H^7 signals are a doublet of AB quartet. [g] Data from ref. 4 for comparison with those for (**4**).

Table 2. Fractional atomic co-ordinates (× 10^4) for [$Os_3H(C_7H_5O)(CO)_9$] (**3**)

Atom	x	y	z	Atom	x	y	z
Os(1)	4 784(1)	6 913(1)	8 436.6(2)	C(3)	2 891(18)	6 722(15)	8 620(7)
Os(2)	5 403(1)	9 656(1)	8 780.5(2)	C(4)	4 395(20)	10 527(17)	8 093(8)
Os(3)	7 663(1)	7 918(1)	8 437.7(2)	C(5)	3 786(16)	9 533(14)	9 213(6)
O(1)	5 210(16)	3 819(12)	8 090(6)	C(6)	6 209(15)	11 390(14)	9 117(6)
O(2)	3 841(14)	7 845(13)	7 151(5)	C(7)	9 437(15)	8 877(16)	8 335(6)
O(3)	1 740(12)	6 585(13)	8 750(6)	C(8)	8 408(18)	6 060(17)	8 609(7)
O(4)	3 799(17)	11 034(14)	7 653(6)	C(9)	7 181(16)	7 433(15)	7 592(7)
O(5)	2 785(13)	9 462(13)	9 486(5)	C(10)	6 330(13)	7 115(13)	9 646(5)
O(6)	6 627(14)	12 403(12)	9 328(6)	C(11)	6 849(14)	8 397(12)	9 340(6)
O(7)	10 482(13)	9 413(13)	8 256(6)	C(12)	8 301(14)	8 825(15)	9 435(6)
O(8)	8 786(14)	4 920(11)	8 718(7)	C(13)	9 503(17)	8 172(15)	9 788(7)
O(9)	7 022(14)	7 141(13)	7 104(5)	C(14)	9 424(18)	7 297(17)	10 290(8)
O(10)	5 328(9)	6 439(9)	9 383(4)	C(15)	8 154(22)	6 697(18)	10 523(7)
C(1)	5 039(16)	4 974(17)	8 228(6)	C(16)	6 806(19)	6 635(17)	10 259(6)
C(2)	4 229(15)	7 500(17)	7 640(8)				

but found none. This and the normal ν(CO) frequencies for an uncharged metal cluster rule out any contribution from this form. However, an equilibrium as shown in Scheme 2 might generate interesting fluxionality and we are pursuing this idea.

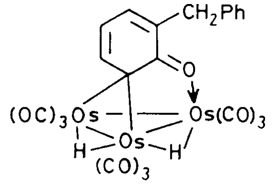
Cluster (**4**), formed as in Scheme 1, is closely analogous to compounds (**6**) and (**7**) which we reported earlier.[4,7,8] I.r. and n.m.r. data support the structure except that there is an unlikely possibility that the CH_2 group is at a position 3 rather than at 7. The final compound, cluster (**5**), is the least well characterised. The formulation [$Os_3(C_7H_8O)(CO)_9$] is clear; the ^{1}H n.m.r.

Table 3. Selected bond lengths (Å) and angles (°) for $[Os_3H(C_7H_5O)(CO)_9]$ (**3**)

Os(2)–Os(1)	2.752(4)	Os(3)–Os(1)	2.873(4)	C(14)–C(13)	1.387(21)	C(15)–C(14)	1.459(25)
Os(3)–Os(2)	2.846(4)	O(10)–Os(1)	2.144(10)	C(16)–C(15)	1.347(26)	C(1)–Os(1)	1.914(18)
C(11)–Os(2)	2.117(15)	C(11)–Os(3)	2.239(13)	C(2)–Os(1)	1.867(18)	C(3)–Os(1)	1.873(19)
C(12)–Os(3)	2.381(14)	C(10)–O(10)	1.239(16)	C(4)–Os(2)	1.899(20)	C(5)–Os(2)	1.872(18)
C(11)–C(10)	1.491(17)	C(16)–C(10)	1.453(18)	C(6)–Os(2)	1.928(15)	C(7)–Os(3)	1.933(16)
C(12)–C(11)	1.423(19)	C(13)–C(12)	1.451(20)	C(8)–Os(3)	1.919(19)	C(9)–Os(3)	1.929(17)

Average C–O (carbonyls) 1.146(20)

Os(3)–Os(1)–Os(2)	60.7(1)	O(10)–Os(1)–Os(2)	84.6(3)	C(16)–C(10)–C(11)	125.9(13)	Os(3)–C(11)–Os(2)	81.5(5)
O(10)–Os(1)–Os(3)	85.8(3)	Os(3)–Os(2)–Os(1)	61.7(1)	C(10)–C(11)–Os(2)	120.1(10)	C(10)–C(11)–Os(3)	112.8(8)
C(11)–Os(2)–Os(1)	74.7(4)	C(11)–Os(2)–Os(3)	51.1(4)	C(12)–C(11)–Os(2)	118.9(10)	C(12)–C(11)–Os(3)	77.6(8)
Os(2)–Os(3)–Os(1)	57.5(1)	C(11)–Os(3)–Os(1)	70.6(4)	C(12)–C(11)–C(10)	121.1(1)	C(11)–C(12)–Os(3)	66.7(8)
C(11)–Os(3)–Os(2)	47.4(3)	C(12)–Os(3)–Os(1)	106.2(4)	C(13)–C(12)–Os(3)	117.2(10)	C(13)–C(12)–C(11)	130.4(13)
C(12)–Os(3)–Os(2)	71.3(4)	C(10)–O(10)–Os(1)	116.6(8)	C(14)–C(13)–C(12)	125.9(15)	C(15)–C(14)–C(13)	128.1(16)
C(11)–C(10)–O(10)	118.5(11)	C(16)–C(10)–O(10)	115.3(13)	C(16)–C(15)–C(14)	129.5(15)	C(15)–C(16)–C(10)	125.7(16)



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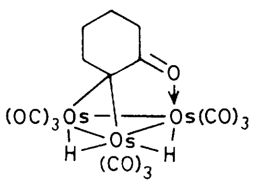

(7)

spectrum showed the expected eight signals and the coupling between these eight protons has been established by full spin decoupling. However, the structure shown is only one of several that are consistent with the C_7H_8O ligand as a six-electron donating μ_3-bridging ligand.

Experimental

Tropone was purchased from Fluka Ltd. and osmium starting materials were made by standard methods.[14]

Reaction of Tropone with $[Os_3H_2(CO)_{10}]$.—A suspension of $[Os_3H_2(CO)_{10}]$ (0.20 g) in cyclohexane (30 cm^3) was treated with tropone (0.2 cm^3) and the mixture heated under reflux for 16 h. The solvent was removed under vacuum and the residue separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)] to give a purple band containing the starting cluster (31%) and two yellow bands which gave $[Os_3H(C_7H_5O)(CO)_{10}]$ (**1**) as yellow crystals (0.020 g, 10%) (Found: C, 21.35; H, 0.8. $C_{17}H_6O_{11}Os_3$ requires C, 21.35; H, 0.65%) and $[Os_3H(C_7H_7O)(CO)_{10}]$ (**2**) as yellow crystals (0.040 g, 16%) (Found: C, 20.75; H, 0.95. $C_{17}H_8O_{11}Os_3$ requires C, 21.3; H, 0.85%).

Reaction at higher temperatures gave decarbonylation. A solution of $[Os_3H_2(CO)_{10}]$ (0.120 g) and tropone (0.1 cm^3) in nonane (15 cm^3) was heated under reflux for 210 min. Removal of solvent and t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–CH_2Cl_2 mixture (7:3 v/v)] gave several bands, the major yellow one yielding $[Os_3H_2(C_7H_6O)(CO)_9]$ (**4**) as orange crystals (0.024 g, 20%).

Reaction of Tropone with $[Os_3(CO)_{10}(MeCN)_2]$.—A solution of tropone (0.2 cm^3) and the bis-acetonitrile cluster (0.22 g) in chloroform (60 cm^3) was heated under reflux for 2 h. Removal of the solvent and chromatographic separation as above gave compound (**1**) (0.050 g, 23%) as yellow crystals. No other tractable product was obtained.

Photolysis of $[Os_3H(C_7H_5O)(CO)_{10}]$ (**1**).—A solution of (**1**) (0.080 g) in cyclohexane (100 cm^3) under an atmosphere of nitrogen at room temperature was irradiated by u.v. light for 1.5 h (Philips 80-W u.v. lamp). Removal of the solvent and chromatography as above gave $[Os_3H(C_7H_5O)(CO)_9]$ (**3**) as very dark red crystals (0.013 g, 17%), while compound (**1**) (0.023 g, 29%) was recovered.

Thermal Treatment of $[Os_3H(C_7H_5O)(CO)_{10}]$ (**1**).—A solution of compound (**1**) (0.094 g) in light petroleum (b.p. 120—160 °C, 50 cm^3) was heated under reflux under nitrogen for 45 min. Removal of the solvent and chromatographic separation gave $[Os_3H(C_7H_5O)(CO)_9]$ (**3**) as orange crystals (0.061 g, 67%) (Found: C, 20.85; H, 0.75. $C_{16}H_6O_{10}Os_3$ requires C, 20.7; H, 0.6%), together with unreacted compound (**1**) (0.003 g, 4%).

Hydrogenation of $[Os_3H(C_7H_5O)(CO)_{10}]$ (**1**).—Hydrogen gas was bubbled at atmospheric pressure through a solution of (**1**) (0.092 g) in refluxing light petroleum (b.p. 120—160 °C, 50 cm^3) for 30 min. The colour of the solution paled from orange to yellow and removal of the solvent and chromatographic separation as above gave several bands of which three gave characterisable compounds: $[Os_3H_2(CO)_{10}]$ (0.009 g, 11%), characterised spectroscopically, $[Os_3H(C_7H_7O)(CO)_{10}]$ (**2**), as yellow crystals (0.002 g, 2%), and $[Os_3H_2(C_7H_6O)(CO)_9]$ (**4**), as orange crystals (0.028 g, 32%) (Found: C, 20.45; H, 0.9. $C_{16}H_8O_{10}Os_3$ requires C, 20.65; H, 0.85%).

Thermal Treatment of $[Os_3H(C_7H_7O)(CO)_{10}]$ (**2**).—A solution of (**2**) (0.011 g) in light petroleum (b.p. 120—160 °C, 25 cm^3) was heated under reflux for 2 h. Removal of the solvent and chromatographic work-up gave three products: $[Os_3H_2(C_7H_6O)(CO)_9]$ (**4**), as yellow crystals (0.005 g, 51%), $[Os_3H_2(CO)_{10}]$ (0.001 g, 11%), and another cluster of formula $[Os_3(C_7H_8O)(CO)_9]$ (**5**) (0.003 g, 29%) (Found: C, 20.9; H, 1.1. $C_{16}H_8O_{10}Os_3$ requires C, 20.7; H, 0.65%).

Crystal Structure Determination.—*Crystal data.* $C_{16}H_6O_{10}Os_3$, $M = 928.82$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $a = 9.417(5)$, $b = 9.470(1)$, $c = 21.989(6)$ Å, $\beta = 95.28(3)°$, $U = 1\,952$ Å^3, $Z = 4$, $D_c = 3.16$ g cm^{-3}, $F(000) = 1\,640$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) 195.6 cm^{-1}; crystal size 0.55 × 0.33 × 0.23 mm.

Data collection. Unit-cell dimensions were determined and intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan procedure[15] to give 3 882 reflections ($3 \leqslant 2\theta \leqslant 50°$). On averaging ($R_{av.} = 0.176$) these yielded 3 433 unique reflections. The segment of reciprocal space scanned was: (h) 0—11, (k) 0—11, (l) −26—26.

Structure solution and refinement. The structure was solved by routine heavy-atom methods. After isotropic refinement of all non-hydrogen atoms the DIFABS method of absorption correction[16] was applied (maximum transmission factor 1.676, minimum value 0.798; $R_{av.} = 0.032$). Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms. The final difference Fourier synthesis did not reveal the position of the bridging hydrogen atom and difficulty was experienced in locating all tropone hydrogen atoms. Thus none was included in the final model. The final values of R and R' were 0.037 and 0.036 respectively for the 262 variables and 2 829 data for which $F^2 > 3\sigma(F^2)$. The function minimised was $\Sigma_w(|F_o| - |F_c|)^2$ with the weight, $w = 1/[\sigma^2(F) + 0.0001\ F^2]$. All computations were made using SHELX 76[17] on a DEC VAX-11/750 computer. The sources of atomic scattering factors and anomalous scattering parameters are as given in ref. 15.

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