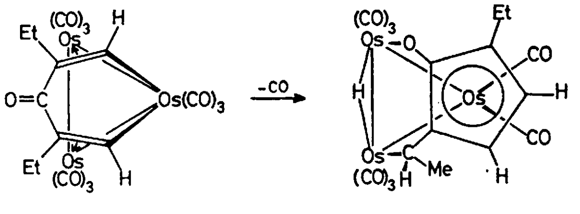
Synthesis and Crystal Structure of $[(\mu_2\text{-H})Os_3(CO)_8\{C(O\text{–})C(CHMe\text{–})CHCHCEt\}]$: a Cluster Compound Containing a μ_3-Trisubstituted-η^5-cyclopentadienyl System

By Melvyn Rowen Churchill* and Romana A. Lashewycz
(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)
and Mamoru Tachikawa and John R. Shapley*
(*Department of Chemistry, University of Illinois, Urbana, Illinois* 61801)

Summary Pyrolysis of the metallocyclohexadienone cluster compound $[Os_3(CO)_9\{(EtC_2H)_2CO\}]$ yields a product of gross stoicheiometry '$Os_3(CO)_9(EtC_2H)_2$,' which has been shown, *via* an *X*-ray structural investigation, to be derived from the starting material *via* a combination of ring contraction to an η^5-cyclopentadienyl system, oxidative addition of an aliphatic C–H bond to the osmium cluster, and loss of a carbonyl ligand.

A CHARACTERISTIC feature of the chemistry of triosmium cluster compounds is the ready scission of C–H bonds in bound hydrocarbon species; however, examples involving aliphatic groups are rare.[1] We have observed a novel example of oxidative addition of an aliphatic C–H bond to a triosmium cluster in which the reactive centre is generated by extrusion of the metal atom from an osmiacyclohexadienone ring.



(1) (2)

Some minor products from the reaction of $[(\mu_2\text{-H})_2Os_3(CO)_{10}]$ with terminal acetylenes have been characterized previously as the metallocyclohexadienone cluster compounds $[Os_3(CO)_9\{(RC_2H)_2CO\}]$. Pyrolysis of $[Os_3(CO)_9\{(EtC_2H)_2CO\}]$ [isomer (**1**)] in refluxing cyclohexane for 3 h cleanly produced a product of gross formula '$Os_3(CO)_9(EtC_2H)_2$.' The ^{1}H n.m.r. spectrum of this product showed clearly that a methylene C–H bond had undergone oxidative addition; $Eu(fod)_3$ addition indicated no remaining ketonic binding site. The nature of the hydrocarbon ligand and the overall stereochemistry of the complex were shown to be as in (**2**) by a single-crystal X-ray diffraction study.

Crystal data: $C_{17}H_{12}O_9Os_3$, M = 930·880, tetragonal, space group $I4_1/a$ [C_{4h}^6; No. 88], a = 26·840(5), c = 11·219(2) Å, U = 8082(2) Å^3, D_c = 3·060 g cm^{-3}, Z = 16, μ(Mo-K_α) = 188·9 cm^{-1}. Diffraction data were collected on a Syntex P2$_1$ diffractometer and the structure was solved *via* a combination of Patterson, difference-Fourier, and least-squares refinement techniques, using a locally modified version of the Syntex XTL system. The final *R*-value was 5·3% for those 2624 independent data in the range 5° $< 2\theta <$ 45° (no datum being rejected). All non-hydrogen atoms were located and refined, the bridging hydride ligand was located on a difference-Fourier synthesis, and all other hydrogen atoms were included in idealized (staggered) positions. The molecular geometry of (**2**) is shown in the Figure.†

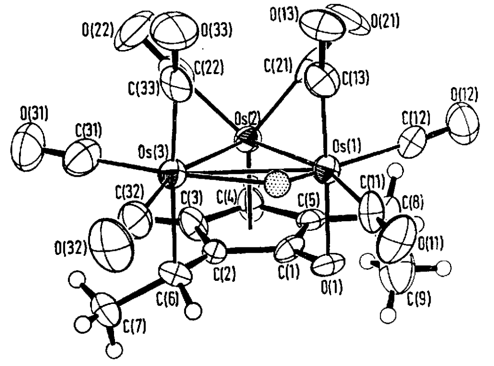


FIGURE. Molecular geometry of $[(\mu_2\text{-H})Os_3(CO)_8\{C(O\text{–})C(CHMe\text{–})\ CHCHCEt\}]$. The bridging hydride ligand is stippled.

The molecule has a central $Os_3(CO)_8$ core with approximate C_s symmetry. Atoms Os(1) and Os(3) are each linked to three terminal carbonyl ligands, while Os(2) is associated with only two such ligands. Extrusion of the osmium atom from the metallocyclohexadienone ring in (**1**) has produced an η^5-cyclopentadienyl unit which is 'π-bonded' directly to Os(2) and which bridges across to atoms Os(1) and Os(3) *via* the systems C(1)–O(1)–Os(1) and C(2)–C(6)–Os(3), in which C(1)–O(1) = 1·303(16) Å, O(1)–Os(1) = 2·138(9) Å, and ∠C(1)–O(1)–Os(1) = 100·1(8)°; and C(2)–C(6) = 1·488(22) Å, C(6)–Os(3) = 2·194(14) Å, and ∠C(2)–C(6)–Os(3) = 96·7(10)°. The μ_2-bridging hydride ligand clearly has been formed by oxidative addition of an aliphatic C–H bond [that involving, originally, C(6)] to the triosmium cluster. While Os(2) formally has a surfeit of bonding electrons, and Os(1) and Os(3) formally have deficits, the triosmium cluster as a whole is associated with the normal 48 bonding electrons.[3]

The non-bridged osmium–osmium distances are normal [Os(1)–Os(2) = 2·819(1) Å and Os(3)–Os(2) = 2·889(1) Å, as compared to Os–Os distances averaging 2·877(3) Å in $Os_3(CO)_{12}$[4]], but the hydrido-bridged osmium—osmium distance is expanded to a value of Os(1)–Os(3) = 3·007(1) Å. This expansion is normal for a metal–metal vector that is spanned by a single unsupported equatorial μ_2-hydride ligand[5] and is consistent with results obtained previously on such triosmium species as $[(\mu_2\text{-H})(H)Os_3(CO)_{11}]$ [Os–(H)–Os

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

= 2·9886(9) Å][4] and [(μ_2-H)(H)$Os_3(CO)_{10}(PPh_3)$] [Os–(H)–Os = 3·0185(6) Å].[6]

Carbon–carbon distances within the carbocyclic ring range from 1·403(23) to 1·463(21) Å and C–C–C angles from 104·9(12) to 110·3(13)°. The ring is planar (r.m.s. deviation = 0·005 Å) and makes an angle of 8·7° with the triosmium plane. Os(2) lies 1·889 Å from the plane of the five-membered ring with an average osmium–carbon distance of 2·251 Å.

Pyrolysis of the other two isomers of [$Os_3(CO)_9\{(EtC_2H)_2CO\}$] (*i.e.*, those with two CH groups or one CH and one CEt groups linked to osmium in the osmiacyclohexadienone ring) indicates a ring contraction reaction similar to that observed for (**1**). This behaviour differs from that of [$Os_3(CO)_9\{(PhC_2H)_2CO\}$], for which carbonyl extrusion from the osmiacyclohexadienone ring has been reported,[2] and adds to the growing complexity of triosmium–acetylene chemistry.[7]

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[1] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727; A. J. Deeming, S. Hasso, and M. Underhill, *ibid.*, 1975, 1614; R. P. Ferrari and G. A. Vaglio, *Gazzetta*, 1975, **105**, 939.

[2] W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organometallic Chem.*, 1975, **88**, C17.

[3] H. D. Kaesz, *Chem. in Britain*, 1973, **9**, 344.

[4] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.

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

[6] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, in the press.

[7] *Cf.*, G. Gervasio, *J.C.S. Chem. Comm.*, 1976, 25, and references therein.