Oxidative Addition of 1,3-Diynes at Triosmium Clusters with Cleavage of the Central Carbon–Carbon Bond: *X*-Ray Crystal Structure of $[Os_3(\mu_3,\eta^2\text{-}C_2Ph)(\mu\text{-}C_2Ph)(CO)_9]$ derived from 1,4-Diphenylbuta-1,3-diyne

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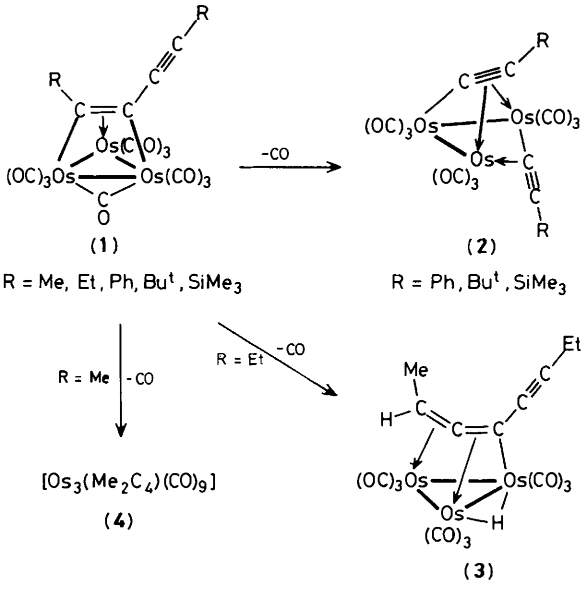
The diyne clusters $[Os_3(\mu_3,\eta^2\text{-}RC{\equiv}CC{\equiv}CR)(CO)_{10}]$ (R = Me, Et, Ph, Bu^t, $SiMe_3$) in hydrocarbon solvent at 120 °C decarbonylate to give the nonacarbonyl clusters $[Os_3(\mu_3,\eta^2\text{-}C_2R)(\mu\text{-}C_2R)(CO)_9]$ when R = Ph, Bu^t, or $SiMe_3$, $[Os_3H(\mu_3,\sigma,\eta^2,\eta^2\text{-}EtC{\equiv}C\text{–}C{=}C{=}CHMe)(CO)_9]$ when R = Et, and $[Os_3(C_4Me_2)(CO)_9]$ of unknown structure when R = Me; the $\mu\text{-}C_2Ph$ ligand in $[Os_3(\mu_3,\ \eta^2\text{-}C_2Ph)(\mu\text{-}C_2Ph)(CO)_9]$ (*X*-ray structure) is unusual in bridging unsymmetrically through only one carbon atom.

Alkynes react with the cluster $[Os_3(CO)_{10}(MeCN)_2]$ to give the triply-bridging alkyne compounds $[Os_3(\mu_3,\eta^2\text{-alkyne})(CO)_{10}]$[1] which thermally decarbonylate to give nonacarbonyl clusters $[Os_3(PhC_2Ph)(CO)_9]$ from diphenylacetylene,[2] $[Os_3H(MeC{=}C{=}CH_2)(CO)_9]$ from but-2-yne,[3] and $[Os_3H(\mu_3,\eta^2\text{-}C{\equiv}CR)(CO)_9]$ from terminal alkynes $RC{\equiv}CH$.[1,3] Except for the diphenylacetylene case, unsaturation resulting from the loss of CO is compensated for by oxidative addition with C–H bond cleavage. Related oxidative additions with C–Cl or C–P cleavage occur in the reactions of $RC{\equiv}CX$ (X = Cl or PPh_2) with $[Ru_3(CO)_{12}]$ to give $[Ru_3(\mu\text{-}X)(\mu_3,\eta^2\text{-}C{\equiv}CR)(CO)_9]$.[4,5] We now report that in the case of 1,3-diynes similar oxidative additions can occur with C–C bond cleavage when there are no suitable C–H or other bonds to be broken. This is the first report of a bis(alkynyl) complex being formed in this way.

The diynes $RC{\equiv}CC{\equiv}CR$ (R = Me, Et, Ph, Bu^t, or $SiMe_3$) react at room temperature with $[Os_3(CO)_{10}(MeCN)_2]$ to give the clusters $[Os_3(\mu_3,\eta^2\text{-}R_2C_4)(\mu\text{-}CO)(CO)_9]$ (**1**) (10—50%) in which only one of the alkyne groups is co-ordinated. We know this because clusters (**1**) are directly analogous spectroscopically to known mono-yne derivatives $[Os_3(\mu_3,\eta^2\text{-}R_2C_2)(\mu\text{-}CO)(CO)_9]$.[1] The ^1H n.m.r. spectrum shows that there are non-equivalent R groups in (**1**) and that the $Os_3(CO)_{10}$ group



Scheme 1

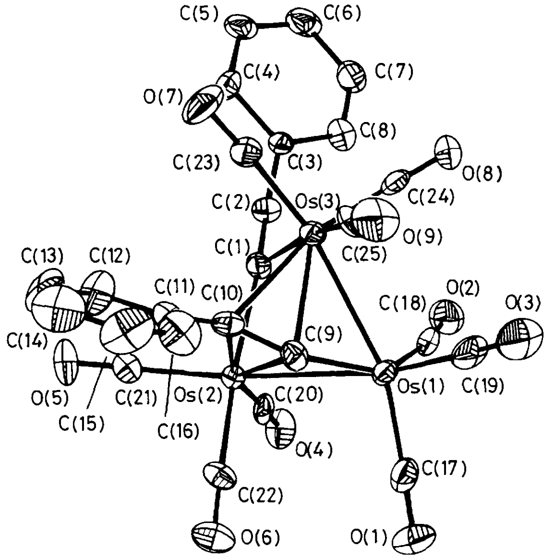


Figure 1. Molecular structure of $[Os_3(\mu\text{-}C_2Ph)(\mu_3,\eta^2\text{-}C_2Ph)(CO)_9]$. Selected dimensions that are not given in Figure 2: Os(1)–Os(2) 2.865(4), Os(1)–Os(3) 2.846(4), Os(2)–Os(3) 3.257(4), Os(1)–C(9) 1.922(18), Os(2)–C(9) 2.235(17), Os(3)–C(9) 2.246(17), Os(2)–C(10) 2.283(19), Os(3)–C(10) 2.297(17), C(9)–C(10) 1.333(22) Å; Os(1)–C(9)–C(10) 152.3(13), C(9)–C(10)–C(11) 141.7(16)°.

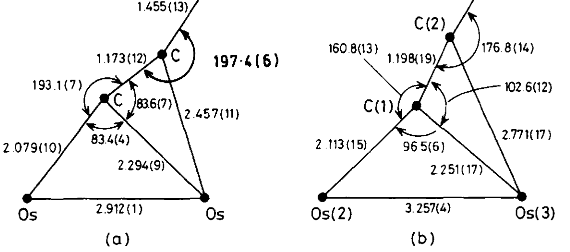


Figure 2. A comparison of the PhC_2 bridges in the two clusters: (a) $[Os_3(\mu,\eta^2\text{-}C_2Ph)(\mu\text{-}AuPMe_2Ph)(CO)_{10}]$ and (b) $[Os_3(\mu\text{-}C_2Ph)(\mu_3,\eta^2\text{-}C_2Ph)(CO)_9]$.

does not rapidly move between the two alkyne groups. In all cases clusters (1) decarbonylate in refluxing light petroleum (b.p. 120—160 °C) to give the nonacarbonyl clusters (2) to (4) with the stoicheiometry $[Os_3(R_2C_4)(CO)_9]$, but the nature of these species depends upon R.

When there are no C–H bonds α to the triple bonds in the diyne, the major product is $[Os_3(C_2R)_2(CO)_9]$ (2) resulting from the cleavage of the central C–C bond of the diyne. The i.r. spectra of clusters (2) (R = Ph, Bu^t, $SiMe_3$) are similar to that of $[Os_3H(C{\equiv}CR)(CO)_9]$ both in the number and frequency of absorptions around 2000 cm^{-1}, so they would seem to have all the same symmetry with H replaced by a symmetrical one-electron donating C_2R group. In the clusters $[Ru_3(\mu\text{-}X)(\mu_3,\eta^2\text{-}C_2R)(CO)_9]$ the Ru–Ru distances associated with the Ru–X–Ru bridge are very dependent upon X: 2.792(3) (X = H),[6] 2.820(1) (X = $AuPPh_3$),[7] 2.900 (X = HgBr),[8] and 3.277 Å (X = Cl).[4] This could reflect the size of X to some extent but also the number of electrons at X available for M–X–M bonding. If X is a one-electron donor a single M–M bond is formally required, but no bond is required if X is a three-electron donor. Alkynyl ligands may be one- or three-electron donor bridging groups and in $[Ru_3(\mu\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)(PPh_2)_2(CO)_5(PPh_2C_2Bu^t)]$ both kinds of bridge are present.[9] A single crystal *X*-ray structure of $[Os_3(C_2Ph)_2(CO)_9]$ was determined† to establish unambiguously that C–C cleavage had occurred and to determine the nature of the alkynyl co-ordination. Figure 1 shows that the two PhC_2 fragments co-ordinate differently; the alkynyl C(9)C(10)Ph co-ordinates in a normal μ_3,η^2-manner but the co-ordination of the alkynyl C(1)C(2)Ph is unusual since it bridges a non-bonded pair of osmium atoms [Os(2)–Os(3) 3.257(4) Å]. The other two osmium–osmium distances are normal for metal–metal bonds. Since there is no Os(2)–Os(3) bond, the alkynyl should be a three-electron donor and we believe that this is correct even though it is not a normal μ,η^2-bridging ligand. Figure 2 compares the geometry of a normal $\mu,\eta^2\text{-}PhC_2$ bridge as found in the cluster $[Os_3(\mu,\eta^2\text{-}C_2Ph)(AuPMe_2Ph)(CO)_{10}]$[10] with that we now find in $[Os_3(PhC_2)_2(CO)_9]$. The Os(3)–C(2) distance is well beyond the normal bonding range [2.771(17) Å] and the PhC_2 ligand may be considered to be co-ordinated through C(1) alone , but it is very unsymmetrical. The geometry is approximately halfway between the normal μ,η^2-mode shown in Figure 2(a) and the normal symmetrical one-electron donating manner. The C_2Ph ligand could be regarded as a three-electron donor with donation through just one carbon atom as in dinuclear aluminium alkynyl species such as $[Al_2Me_4(MeC_2)_2]$[11] and $[Al_2Ph_4(PhC_2)_2]$.[12] This appears to be the first transition metal example of this arrangement.

Hydrogenation of $[Os_3(C_2Ph)_2(CO)_9]$ (1 atm, octane, 125 °C) gave $[Os_3H_3(\mu_3\text{-}CCH_2Ph)(CO)_9]$ (17%) but we cannot tell which of the alkynyl ligands has been displaced from the cluster. The thermal decarbonylation of $[Os_3(Et_2C_4)(CO)_{10}]$ (1) leads to hydrido-complex (3) (Scheme 1) and we assume that the availability of C–H bonds adjacent to the alkyne group allows their cleavage in preference to C–C cleavage. However, the hexa-2,4-diyne compound $[Os_3(Me_2C_4)(CO)_{10}]$ decarbonylates to the non-hydrido species (4). Spectroscopic data‡ for (4) indicate that it is not related to compounds (2).

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† *Crystal data* for (2; R = Ph): $C_{25}H_{10}O_9Os_3$, *M* = 1024.9, monoclinic, space group *C*2/*c* (No. 15), *a* = 16.956(6), *b* = 9.950(2), *c* = 30.790(6) Å, β = 95.88(2)°, *U* = 5167 $Å^3$. *Z* = 8, D_c = 2.635 g cm^{-3}, *F*(000) = 3680, λ = 0.71069 Å, μ(Mo-K_α) = 147.9 cm^{-1}, crystal dimensions 0.73 × 0.55 × 0.48 mm. The structure was solved by the heavy atom technique and refined by full-matrix least-squares using absorption corrected data. Measurements were made on a CAD4 diffractometer using Mo-K_α radiation (graphite monochromator) $3 \leqslant 2\theta \leqslant 50°$, *h* (−20 → 20) *k*(0 → 12) *l*(0 → 38), 5474 reflections were observed, 3861 of which were independent [$I \geqslant 3\sigma(I)$]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms placed in calculated positions (C–H 0.96 Å, *U* = 0.10 $Å^2$); 334 parameters refined. The final residuals *R* and R_w were 0.049 and 0.050 respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *Key spectroscopic data* (i.r. in hexane; ^1H n.m.r. in $CDCl_3$ at 25 °C at 200 MHz). Compound (2; R = Ph): ν(CO) 2092w, 2072vs, 2046vs, 2011vs, 2001s, 1976m, 1943vw cm^{-1}. (2; R = Bu^t): ν(CO) 2089w, 2067vs, 2044vs, 2010vs, 1997vs, 1973m, 1942vw cm^{-1}; ^1H n.m.r. δ 1.57(s) and 1.13(s). (2; R = $SiMe_3$): ν(CO) 2092m, 2067vs, 2045vs, 2010vs, 2001vs, 1978vs, 1972vs, 1940w cm^{-1}; ^1H n.m.r. δ 0.50(s) and 0.17(s). Compound (3): ν(CO) 2095s, 2070vs, 2045vs, 2022vs, 2011s, 2002s, 1992m, 1982m, 1952vw cm^{-1}; ^1H n.m.r. δ 3.25 (q, *J* 5.4 Hz), 2.40 (q, *J* 7.4 Hz), 2.05 (d, *J* 5.4 Hz), 1.14 (t, *J* 7.4 Hz), −21.75 (s). Compound (4): ν(CO) 2097w, 2071vs, 2045vs, 2038vs, 2014s, 2001s, 1973m cm^{-1}; ^1H n.m.r. δ 3.67 (s) and 2.11 (s).

The i.r. spectrum (ν_{CO}) is significantly different while the two methyl ^1H n.m.r. singlets at δ 3.67 and 2.11 do not support a structure like that of $[Os_3(PhC_2)_2(CO)_9]$. We are trying to obtain crystals suitable for *X*-ray structure determination; the low field signal at δ 3.67 is very low and close to the μ_3-CMe signals for known compounds. At present we do not know the structure of this nonacarbonyl derivative.

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