Novel Linkage of Two Molecules of Phenylacetylene in an Osmium Cluster Compound: Molecular Structure of μ_3-(4–6-η-2,5-Diphenyl-3-oxahexa-1,5-diene-1,4,6-triyl)-μ-carbonyl-octacarbonyl-*triangulo*-triosmium(3-*Os–Os*)

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Summary The molecular structure of the title compound obtained from the reaction of $Os_3(CO)_{12}$ with phenylacetylene reveals the unique feature of two alkyne molecules linked through a carbon and an oxygen atom derived from opening of the C=O bond of a carbonyl group; two five-membered rings are formed with σ and π bonds to the Os_3 cluster, and a highly asymmetrical bridging carbonyl group is present.

As a part of structural study on acetylene derivatives of $Os_3(CO)_{12}$,[1] we carried out the *X*-ray analysis of the compound of formula $Os_3(CO)_{10}(HC_2Ph)_2$ obtained from $Os_3(CO)_{12}$ and phenylacetylene.[2]

Crystal data: $C_{26}H_{12}O_{10}Os_3$, orthorhombic, space group $P2_12_12_1$, $a = 20{\cdot}10(1)$, $b = 15{\cdot}30(1)$, $c = 8{\cdot}57(1)$ Å, $Z = 4$; the intensities were recorded with ω–2θ scanning and Mo-K_α radiation, on a Siemens four-circle automatic diffractometer. The structure (Figure) was solved by the Patterson method and subsequent Fourier-differences. Refinement by least-squares, using 2587 reflections, led to $R = 0{\cdot}086$ (weighted $R = 0{\cdot}088$).

The three osmium atoms form a triangle in which Os(1)–Os(2) = 2·794(2), Os(1)–Os(3) = 2·857(2), and Os(2)–Os(3) = 2·880(2) Å. Eight terminal carbonyl groups occupying equatorial and axial positions are bonded to the three osmium atoms; one CO asymmetrically bridges the Os(2)–Os(3) bond. In the terminal carbonyl groups the mean Os–C and C–O distances are 1·90(5) and 1·16(6) Å respec-

tively; the values, Os(2)–C = 2·30(4), Os(3)–C = 1·86(3), and C–O = 1·19(7) Å, compare well with the reported distances for grossly unsymmetrical CO bridges.[3]

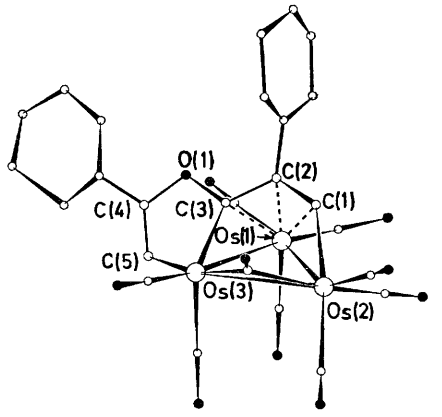

FIGURE. Bond lengths: C(1)–C(2), 1·50(4); C(2)–C(3), 1·29(5); C(3)–O(1), 1·45(4); O(1)–C(4), 1·43(4); C(4)–C(5), 1·36(5) Å.

The novel and most interesting feature of this structure is the unusual linkage between the two phenylacetylene groups through a carbon and an oxygen atom [C(3) and O(1)] derived from the opening of a carbonyl C=O bond. Two five-membered rings are hence joined along the C(3)–Os(3) bond.

Atoms C(1), C(2), and C(3) are equidistant from Os(1) at 2·30(4) Å, while the Os(2)–C(1), Os(3)–C(3), and Os(3)–C(5) bonds are 2·05(3), 2·10(4), and 2·05 (4) Å respectively. These and other data (Figure) are consistent with there being π-bonding between Os(1) and the allylic carbon atoms C(1), C(2), and C(3), and σ-bonding between C(1) and Os(2), and C(3) and C(5) and Os(3). Os(2)–C(1), Os(3)–C(3), and Os(3)–C(5) are only slightly greater than the mean Os–CO bond length indicating a partial double bond character [*cf.* $HRu_3(CO)_9PhCC_6H_4$,[4] $HRu_3(CO)_9C_{12}H_{15}$,[5] and $HRu_3(CO)_9C_6H_9$[6]].

The planarity of the two five-membered rings [Os(2)-Os(3)C(1)C(2)C(3) and Os(3)C(3)O(1)C(4)C(5) planes form an angle of *ca.* 20°], and the bond angles value confirm a structure similar to that suggested[7] for $HRu_3(CO)_9PhCC_6H_4$ with a partial carbenic character of C(1), C(3), and C(5). While for the Os(2)Os(3)C(1)C(2)C(3) ring a delocalized π system is an apposite description, the C–C and C–O distances in the Os(3)C(3)O(1)C(4)C(5) ring are more consistent with a double and a single bond respectively; the present stage of refinement, however, allows no thorough discussion about the bond order between the light atoms.

In the light of this analysis the title compound can be formulated as $Os_3(CO)_9(HC_2PhCOCPhCH)$.

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