

Synthesis and Structure of the Planar Metal Carbonyl Os₅(CO)₁₈

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The new binary metal carbonyl Os₅(CO)₁₈ has been prepared by pyrolysis of Os₅(CO)₁₉ and shown by X-ray crystallography to have a planar metal skeleton.

A fundamental aspect of metal cluster chemistry is the geometry or geometries that are adopted by a cluster of a given nuclearity and electron count. Here we describe the synthesis and structure of Os₅(CO)₁₈ **1** a hitherto missing member of the pentanuclear binary carbonyls of osmium [Os₅(CO)₁₉^{1,2} and Os₅(CO)₁₆³ have previously been prepared by Lewis, Johnson and co-workers]. The structure of **1**, an 76-electron cluster, reveals it has a planar, 'raft-like' arrangement of metal atoms rather than the bent structure that had been assumed.²

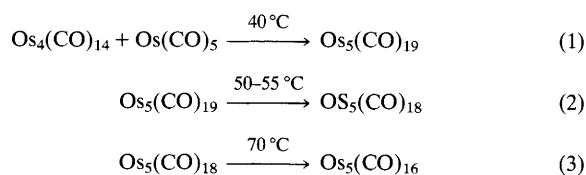
The reaction of Os₄(CO)₁₄⁴ and Os(CO)₅⁵ in CH₂Cl₂-hexane at 40 °C for 24 h afforded the known Os₅(CO)₁₉ **2**¹ in 63% yield after chromatography. Pyrolysis of **2** in CH₂Cl₂ contained in a sealed, evacuated flask at 50–55 °C for 3 days gave **1** [Scheme 1, eqns. (1) and (2)]. The cluster was isolated in 78% yield after chromatography and recrystallisation as deep-red, air-stable crystals.[†]

The structure of **1** was solved by X-ray crystallography;‡ a view of the molecule is shown in Fig. 1. As can be seen from Fig. 1, **1** has a planar, raft-like arrangement of osmium atoms. It therefore resembles Os₆(CO)₁₇[P(OMe)₃]₄⁶ and Os₃Pt₂(CO)₁₄.⁷ The seven Os–Os bond lengths in **1** range from 2.847(1) to 2.892(1) Å (Fig. 1), consistent with Os–Os single bonds. An unusual feature of the structure of **1** is the presence of a bridging carbonyl [Os(2)–C(0) 2.23(3); Os(3)–C(0) 1.99(3) Å], so that in the solid state the molecule has approximate C_{2v} symmetry.

‡ Crystal data for **1**: C₁₈O₁₈Os₅, *M* = 1455.2, triclinic, space group *P* $\bar{1}$, *a* = 8.866(2), *b* = 10.311(2), *c* = 15.527(3) Å, α = 73.71(1), β = 83.99(2), γ = 71.06(1)°, *Z* = 2, *D*_c = 3.751 g cm⁻³, scan mode ω -2 θ , θ_{\max} = 23°, μ (Mo-K α) = 246.78 cm⁻¹, *R* = 0.039 from 2474 reflections [*I* > 2.5 σ (*I*)] and 191 parameters.

Data were collected at room temp. on an Enraf Nonius CAD-4 diffractometer using graphite-monochromated Mo-K α radiation; the data were corrected for absorption. The Os atoms were located by direct methods and subsequent electron density difference synthesis revealed the remaining atoms. Atomic coordinates, thermal parameters, and bond lengths and angles for **1** have been deposited at the University of Bonn, Germany. See Notice to Authors, Issue No. 1.

† **1**: Satisfactory elemental analyses were obtained; *m/z* (FAB) 1455.6 (vw, M⁺); IR (CH₂Cl₂, ν/cm⁻¹): ν(CO) 2097(s), 2075(m), 2073(m), 2046(s), 2027(m), 2002(w), 1936(w) and 1832 (w, br).



Scheme 1

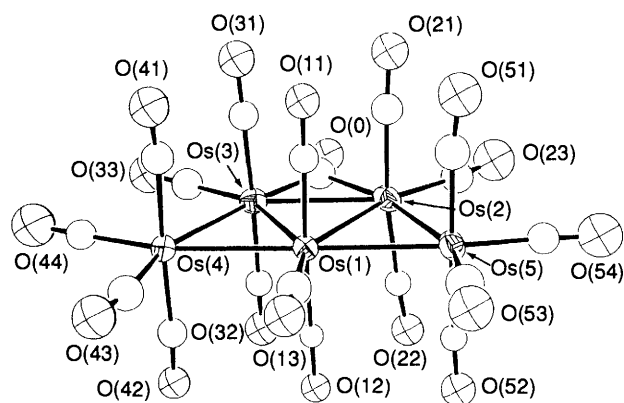


Fig. 1 The molecular structure of $\text{Os}_5(\text{CO})_{18}$. Metal-metal bond lengths: Os(1)–Os(2), 2.860(1); Os(1)–Os(3), 2.860(1); Os(1)–Os(4), 2.850(1); Os(1)–Os(5), 2.878(1); Os(2)–Os(3), 2.847(1); Os(2)–Os(5), 2.853(1); Os(3)–Os(4), 2.892(1) Å.

After the Os atoms were refined anisotropically and all light atoms isotropically, the difference map revealed two extended peaks, one $[2.3(3) \text{ e } \text{Å}^{-3}]$ at 2.9 Å from Os(2) and Os(5) and the second $[2.0(3) \text{ e } \text{Å}^{-3}]$ at 2.8 Å from Os(3) and Os(4). Furthermore, there was greater thermal motion of all the equatorial carbonyl ligands compared to their axial counterparts. These results are interpreted in terms of a small amount (<10%) of a second form of **1** with bridging carbonyls across these Os–Os bonds. In CH_2Cl_2 , a solvent in which it is only sparingly soluble, **1** exhibits only a very weak IR absorption in the region expected for a bridging CO ligand. In this respect it therefore resembles its more famous relative $\text{Fe}_3(\text{CO})_{12}$.⁸

Heating of **1** in CH_2Cl_2 in a closed, evacuated flask above 70 °C caused its conversion to $\text{Os}_5(\text{CO})_{16}$ with no evidence by

IR spectroscopy for $\text{Os}_5(\text{CO})_{17}$. While $\text{Os}_5(\mu\text{-H})_2(\text{CO})_{16}$ has an edge-bridged tetrahedral arrangement of metal atoms,⁹ it does not necessarily follow that $\text{Os}_5(\text{CO})_{17}$, if it could be prepared, will have the same arrangement. We have shown that $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}(\text{PMe}_3)$ has a nonplanar butterfly configuration of osmium atoms whereas in $\text{Os}_4(\text{CO})_{14}(\text{PMe}_3)$ the metal atoms are essentially planar.¹⁰

Both $\text{Os}(\text{CO})_5$ and $\text{Os}_4(\text{CO})_{14}$ are prepared from $\text{Os}_3(\text{CO})_{12}$.^{4,5} The reactions shown in eqns. (1)–(3) therefore represent the systematic synthesis of the pentanuclear carbonyl clusters of osmium, and builds on our earlier studies on the synthesis of the tetranuclear congeners.¹¹

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