Diosmium Enneacarbonyl

By J. R. Moss and W. A. G. Graham*
(*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada*)

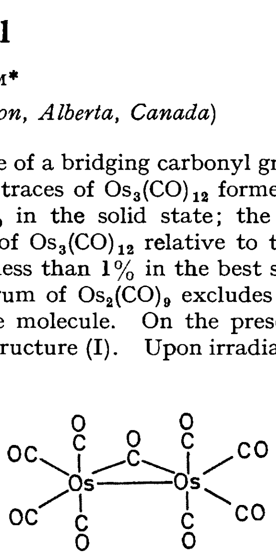
Summary Diosmium enneacarbonyl, $Os_2(CO)_9$, has been prepared by u.v. irradiation of osmium pentacarbonyl at $-40°$.

ALTHOUGH di-iron enneacarbonyl was prepared 65 years ago,[1] its ruthenium and osmium analogues have been elusive. Substances formulated initially as $Ru_2(CO)_9$[2] and $Os_2(CO)_9$[3] were later shown by *X*-ray crystallography to be $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.[4] As a recent reviewer has put it, "The existence of $Ru_2(CO)_9$ and $Os_2(CO)_9$ seems to be *sub judice*."[5]

We now report the preparation of $Os_2(CO)_9$ by u.v. irradiation of an n-heptane solution of $Os(CO)_5$ at $-40°$.[6] The orange-yellow, crystalline compound is conveniently separated from $Os_3(CO)_{12}$ by sublimation at room temperature in high vacuum on to a $-20°$ probe, and melts with decomposition at 64—67°. Unlike $Fe_2(CO)_9$, $Os_2(CO)_9$ is soluble in hydrocarbon solvents. The compound is somewhat light-sensitive and less stable thermally than $Fe_2(CO)_9$; it decomposes both in solution (half life *ca.* 1 hr. at room temperature) and more slowly in the solid state. Terminal carbonyl stretching bands are observed in the i.r. spectrum at 2080 s, 2038 vs, 2024 m, 2013 s, and 2000 w, with a single bridging band at 1778 m (cm^{-1}, n-heptane).

The mass spectrum shows the molecular ion at *m/e* 634, having the isotope pattern expected for Os_2, and the successive loss of nine carbonyl groups. Peaks due to the series $[Os(CO)_n]^+$ ($n = 0$—5) are also observed, consistent with the presence of a bridging carbonyl group.[7] The mass spectrum shows traces of $Os_3(CO)_{12}$ formed by decomposition of $Os_2(CO)_9$ in the solid state; the intensity of the strongest peaks of $Os_3(CO)_{12}$ relative to those of $Os_2(CO)_9$ is variable, and less than 1% in the best samples.

The i.r. spectrum of $Os_2(CO)_9$ excludes an $Fe_2(CO)_9$-like structure for the molecule. On the present evidence, we favour the C_{2v} structure (I). Upon irradiation of a heptane solution of $Os(CO)_5$ in an i.r. cell at $-30°$, bands of $Os_2(CO)_9$ and $Os_3(CO)_{12}$ appeared. When $Ru(CO)_5$ was similarly irradiated, bands appeared [in addition to those of $Ru_3(CO)_{12}$] which resembled those of $Os_2(CO)_9$, and which may be attributed to $Ru_2(CO)_9$. Because of its much lower stability, $Ru_2(CO)_9$ has not yet been isolated.



(I)

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