Dihydrido-octacarbonyldiosmium and Some Derivatives

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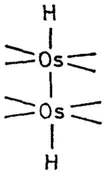
Summary The first binuclear carbonyl hydride of osmium, $H_2Os_2(CO)_8$, has been prepared and converted into $Cl_2Os_2(CO)_8$, $Br_2Os_2(CO)_8$, and $H_2Os_2(CO)_6(PPh_3)_2$.

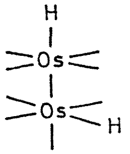
OSMIUM complexes containing only hydrogen and carbon monoxide as ligands have been characterized only recently. Mononuclear $H_2Os(CO)_4$,[1] trinuclear $H_2Os_3(CO)_{10}$,[2] and the tetranuclear species $H_4Os_4(CO)_{12}$ and $H_2Os_4(CO)_{13}$[2] have thus far been reported. We now describe the preparation and characterization of a *binuclear* carbonyl hydride, $H_2Os_2(CO)_8$.

The carbonylation of osmium tetroxide in the presence of hydrogen has been reported to give $H_2Os(CO)_4$ in high yield.[1] We find that $H_2Os_2(CO)_8$ is also formed in this reaction, although in rather low yields (*ca.* 10—15%); its lower volatility permits a convenient separation from the major reaction product. At room temperature, $H_2Os_2(CO)_8$ is a colourless, slightly volatile oil. The mass spectrum exhibits the molecular ion (calculated *m/e* 607·8952; found, 607·8889) and a successive loss of eight carbonyl groups. The ^1H n.m.r. spectrum (benzene solution) shows a sharp singlet at τ 20·11, suggesting that the two hydrogens in the molecule are equivalent, excluding the possibility of a rapid exchange process.

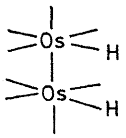
The i.r. spectrum shows five strong carbonyl stretching bands with additional weak bands (see Table). The highly symmetrical structure (I) can therefore be excluded. If (II) is excluded on the n.m.r. evidence, structure (III) or one of its conformers remains as the most probable arrangement.



(I)



(II)



(III)

TABLE

I.r. bands in the carbonyl stretching region (heptane solution)

Compound	Bands (cm.$^{-1}$) with relative intensities
$H_2Os_2(CO)_8$	2132 vw, 2093 s, 2057 vs, 2039 vs, 2033s, 2023 sh, 2020 s, 1988 vw.
$Cl_2Os_2(CO)_8$	2121 s, 2082 vs, 2069 s, 2064 s, 2054 s, 2032 s.
$Br_2Os_2(CO)_8$	2118 s, 2080 vs, 2068 s, 2063 s, 2052 s, 2031 s.
$H_2Os_2(CO)_6(PPh_3)_2$[a]	2109 vw, 2073 w, 2029 sh, 2008 vs, 1979 s, 1959 sh, 1915 w, broad.

[a] Measured in dichloromethane.

The new hydride reacts quantitatively with CCl_4 or CBr_4 affording the dihalides $X_2Os_2(CO)_8$ (X = Cl, Br). The di-iodide of this series has very recently been reported as a product of the reaction of CF_3I or iodine with $Os_3(CO)_{12}$.[3] Mass spectra of the dihalides show the molecular ion, successive loss of eight carbonyl groups, then the loss of two halogens. The carbonyl stretching bands of the dihalides (Table) resemble those of $H_2Os_2(CO)_8$, suggesting a close structural relation to the present hydride.

Triphenylphosphine (2 moles) reacts with $H_2Os_2(CO)_8$ to form colourless, crystalline $H_2Os_2(CO)_6(PPh_3)_2$, m.p. 207—210°. The n.m.r. spectrum of this complex shows a high-field resonance pattern of AA′XX′ type centred at τ 19·46 (CH_2Cl_2 solution), with the separation of the major doublet $|J_{H\text{-}Os\text{-}P} + J_{H\text{-}Os\text{-}P}| = 18{\cdot}5$ Hz.

(*Received, May 29th, 1969; Com.* 753.)

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[3] M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc.* (*A*), 1969, 987.