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## Preliminary communication

# New carbonyl hydrides of osmium and a suggested intermediacy of $Os(CO)_4$ in their formation

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Osmium carbonyl chemistry has burgeoned in the last few years with the discovery of convenient synthetic methods for such fundamental starting materials as $Os_3(CO)_{12}$ [1,2] and $H_2Os(CO)_4$ [3]. We reported recently that the reaction of osmium tetroxide with carbon monoxide and hydrogen afforded, in addition to $H_2Os(CO)_4$, the dinuclear dihydride $H_2Os_2(CO)_8$ [4]. The latter appears to be the first well-characterized polynuclear carbonyl hydride which can be assumed without ambiguity to possess a terminal metal–hydrogen bond[★]; as we suggest below, this feature may be of importance in the chemical reactions of such compounds.

We wish first to report that a trinuclear homologue, $H_2Os_3(CO)_{12}$, has now been isolated from the same reaction. It is an air-stable, almost colorless crystalline solid, m.p. 95–98°, characterized by analysis and mass spectrum. The latter exhibits the molecular ion (calculated $m/e$, 909.834; observed, 909.828) with the expected isotope pattern. A sharp singlet at $\tau$19.85 is observed in the NMR spectrum in benzene solution, while the infrared spectrum (n-heptane) shows bands in the carbonyl stretching at 2135vvw, 2100s, 2070w, 2053s, 2043sh, 2038s, 2030vs, 2022s, 2003sh, 1995m, 1991sh cm$^{-1}$; in a saturated solution, very weak broad bands become visible at 1963 and 1950 cm$^{-1}$. The complex infrared spectrum excludes a linear or all-*trans* structure of $D_{4h}$ symmetry, but does not differentiate among a number of less symmetrical possibilities. In view of the stereochemically nonrigid character of metal carbonyl hydrides[6-8], the single NMR band must also be interpreted with caution.

Further confirmation of this new hydride is provided by its reaction with $CCl_4$ or $CBr_4$, affording the known dihalides $Os_3(CO)_{12}X_2$ [2]. Carbonyl stretching frequencies of the dihalides, not reported previously[2], are as follows: X = Cl, 2150w, 2120s, 2085w (sh), 2063vs, 2030s, 2001m; X = Br, 2148w, 2118s, 2086w (sh), 2062vs, 2032s, 2002m cm$^{-1}$; the spectra were taken in dichloromethane. Both of these dihalides can be reduced to

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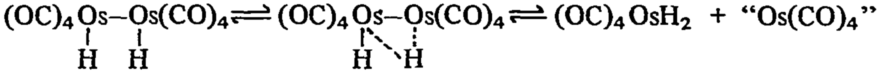
[★] By "polynuclear carbonyl hydride" we mean a compound of the general formula $H_xM_y(CO)_z$. Less strictly, the compounds $(\pi\text{-}C_5H_5)_2MH_2M(CO)_5$ (M = Cr, Mo, W)[5] exhibit this structural feature, although the metal–metal bond is of the coordinate covalent type.

$H_2Os_3(CO)_{12}$ with sodium borohydride in methanol, although in poor yield. This may be contrasted with the reduction of $Os_3(CO)_{12}Cl_2$ using sodium borohydride in tetrahydrofuran, reported to form $HOs_3(CO)_{10}Cl$ in low yield[9].

With a view to elucidating the processes involved in the hydrocarbonylation of osmium tetroxide, the thermolysis of $H_2Os_3(CO)_{12}$ has been studied at 120° in sealed tubes without solvent. The reaction produced a mixture of the osmium carbonyl dihydrides $H_2Os(CO)_4$, $H_2Os_2(CO)_8$, and $H_2Os_3(CO)_{12}$, as well as $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{12}$. Thermolysis of $H_2Os_2(CO)_8$ affords the same mixture of dihydridocarbonyls. We have also obtained mass spectrometric evidence for the presence of $H_2Os_4(CO)_{16}$ in the thermolysis products. This tetranuclear hydride would be the fourth member of the series $H_2[Os(CO)_4]_n$ ($n = 1, 2, 3$ or 4). Presumably higher members are formed as well, but are present in low concentration.

We suggest that the thermolysis products can be accounted for by a mechanism involving elision of an $Os(CO)_4$ group from the initial di- or tri-nuclear hydride. This process can be visualized as a 1,2-shift of hydrogen, *e.g.*,



$$(OC)_4\underset{H}{Os}-\underset{H}{Os}(CO)_4 \rightleftharpoons (OC)_4\underset{H\ \ H}{Os-Os}(CO)_4 \rightleftharpoons (OC)_4OsH_2 + \text{“}Os(CO)_4\text{”}$$

The coordinatively unsaturated $Os(CO)_4$ species could reinsert into an Os–H bond of $H_2Os(CO)_4$, regenerating the dinuclear species; or, by insertion into Os–H of $H_2Os_2(CO)_8$, it would form the trinuclear species. The latter could also produce $Os(CO)_4$, or react with it to form $H_2Os_4(CO)_{16}$. The novelty resides not in the intermediate itself, but in the mechanism proposed for its formation.

Consistent with this suggestion, thermolysis of $H_2Os_3(CO)_{12}$ in the presence of rhenium pentacarbonyl hydride affords the new mixed metal compound $(OC)_5ReOs(CO)_4H$, in addition to the usual mixture of osmium carbonyl hydrides. Complete separation from $H_2Os_2(CO)_8$ is difficult, and a pure sample of $(OC)_5ReOs(CO)_4H$ has not yet been obtained. The mass spectrum shows the parent ion of the mixed-metal hydridocarbonyl species with the expected isotope pattern, and an NMR signal is observed at $\tau 20.37$ in benzene. An additional observation consistent with the elision mechanism is the formation of $(C_6H_5)_3POs(CO)_4$ as a byproduct in the reaction between $(C_6H_5)_3P$ and $H_2Os_2(CO)_8$, which afforded $H_2Os_2(CO)_6[P(C_6H_5)_3]_2$ as the main product[4]. Further studies are in progress to test this mechanism, and to exclude, if possible, an alternate one involving homolytic cleavage of osmium–osmium bonds, *i.e.*, a radical mechanism.

It is of interest that a solution of $H_2Os(CO)_4$ in n-heptane when heated to 100° produces a single product, pale yellow in color, which has been characterized by mass spectrometry and analysis as $H_4Os_4(CO)_{12}$. Infrared bands are observed in cyclohexane at 2085s, 2068vs, 2022vs and 2000m $cm^{-1}$. A compound of the same molecular formula has been reported[2], but the infrared spectrum establishes that a different isomer has been produced in the present work.

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## REFERENCES

1 C.W. Bradford and R.S. Nyholm, *Chem. Commun.*, (1967) 384.
2 B.F.G. Johnson, J. Lewis and P.A. Kilty, *J. Chem. Soc., A*, (1968) 2859.
3 F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 6 (1967) 2092.
4 J.R. Moss and W.A.G. Graham, *Chem. Commun.*, (1969) 800.
5 B. Deubzer and H.D. Kaesz, *J. Amer. Chem. Soc.*, 90 (1968) 3276.
6 J.W. Faller, A.S. Anderson and C. Chen, *Chem. Commun.*, (1969) 719.
7 W.J. Miles, Jr. and R.J. Clark, *Inorg. Chem.*, 7 (1968) 1801.
8 F.N. Tebbe, P. Meakin, J.P. Jesson and E.L. Muetterties, *J. Amer. Chem. Soc.*, 92 (1970) 1068.
9 A.J. Deeming, B.F.G. Johnson and J. Lewis, *J. Organometal. Chem.*, 17 (1969) P40.