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Preliminary communication

TRI- AND DI-NUCLEAR OSMIUM COMPLEXES DERIVED FROM $H_2Os_3(CO)_{10}$ AND SUBSTITUTED ACETYLENES

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Summary

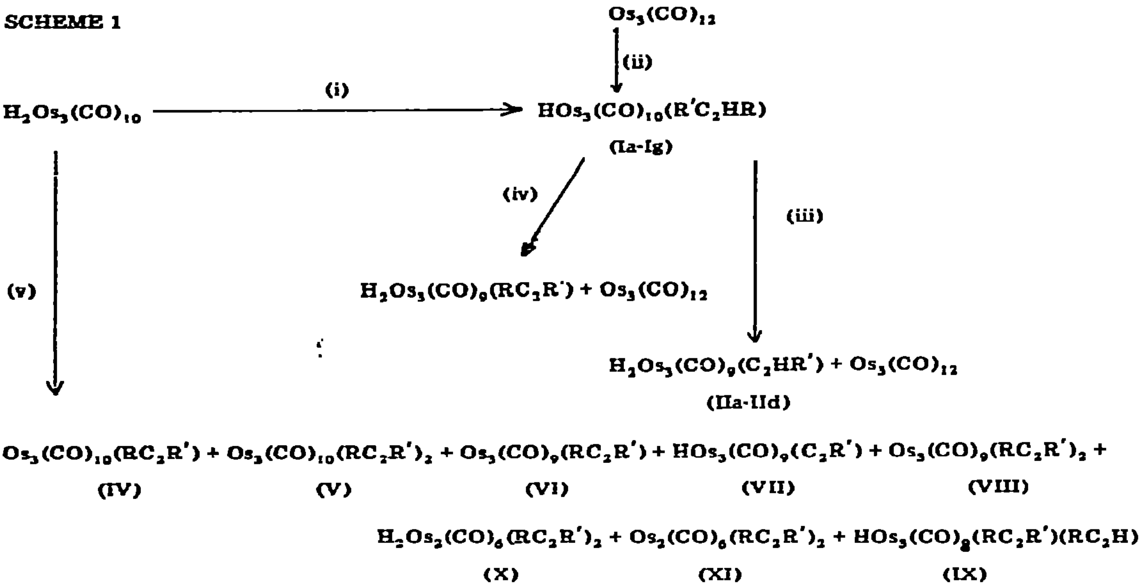
The reaction of $H_2Os_3(CO)_{10}$ with acetylenes to give organoosmium cluster derivatives are reported.

The reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with alkynes or alkenes have afforded a wide variety of organometallic compounds [1]. More recent studies [2, 3] employing the hydrido complexes $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$ and $H_2Os_3(CO)_{10}$ have provided additional compounds previously inaccessible from the simple carbonyls. We report here preliminary studies of the reactions of $H_2Os_3(CO)_{10}$ with simple mono- and di-substituted acetylenes (see Scheme 1).

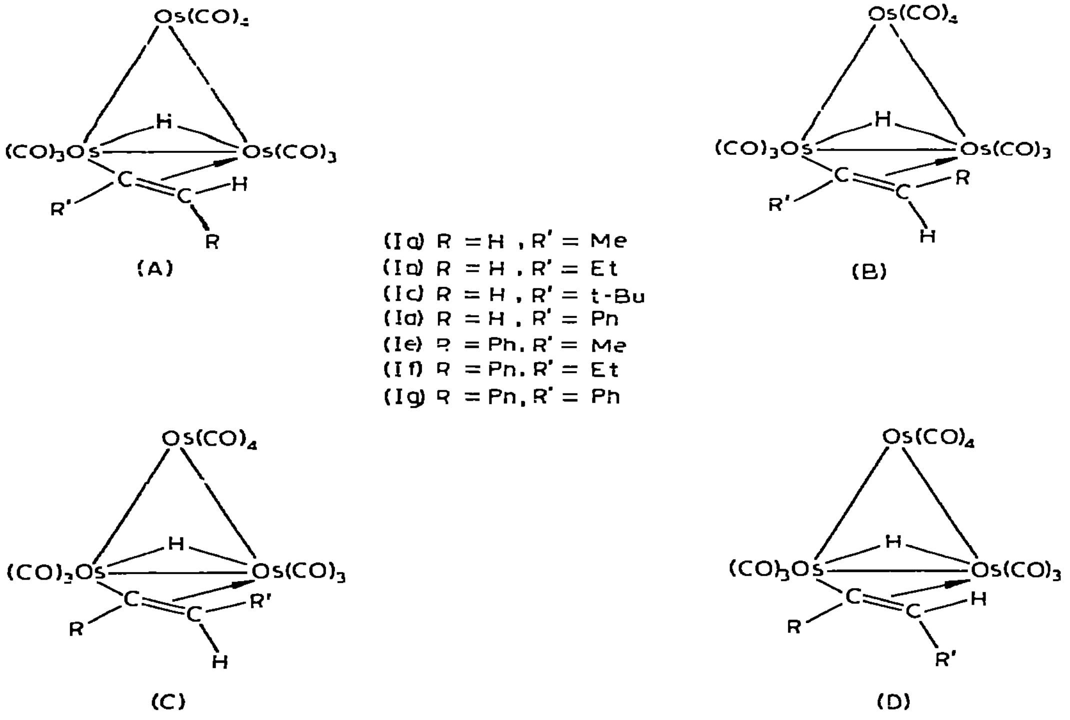
The dihydride $H_2Os_3(CO)_{10}$ reacts with RC_2R' in n-hexane (ca. 3 h, 20°) to give bridged complexes of the type $HOs_3(CO)_{10}RC_2HR'$ (Fig. 1), which are analogous to the simple acetylene derivative (R = R' = H) obtained by the reaction of C_2H_2 with $H_2Os_3(CO)_{10}$. For complexes Ia-If four isomeric types are possible, A-D, and for complex Ig two, C and D. The ^1H NMR spectra of complexes Ia-Id, which show no temperature dependence over the range −80 to +60°C, clearly establish that only isomeric form D is present. We have been unable to differentiate between the two possibilities C or D for Ig. On heating in n-octane, compounds Ia-Id eliminate CO to produce complexes IIa-IId in which the organo group spans three osmium atoms and an H-atom has migrated from the CHR'=CR group to the Os_3 cluster (Fig. 2). Compound Ig also eliminates CO on heating but the complex III obtained has the alternative structure shown (Fig. 2). Similar complexes have been prepared previously from the reaction of $M_3(CO)_{12}$ (M = Ru or Os) and RCH=CHR', RR'C=CH_2 or RHC=CH_2 [3]. The present work supports the view that complexes I are the unobserved intermediates in these reactions.

Other products may be obtained from these reactions particularly at higher acetylene concentrations and over longer periods: $Os_3(CO)_{10}(RC_2R')$ (IV);

SCHEME 1



(i) Reaction with RC_2R' in n-hexane at 20°C; (ii) Reaction with C_2H_4 (unobserved intermediate); (iii) Heating in n-octane under reflux, applies only to complexes Ia-Id; (iv) Heating Ig in n-octane under reflux; (v) Reaction with excess of the acetylene.



(Ia) R = H, R' = Me
(Ib) R = H, R' = Et
(Ic) R = H, R' = t-Bu
(Id) R = H, R' = Ph
(Ie) R = Ph, R' = Me
(If) R = Ph, R' = Et
(Ig) R = Ph, R' = Ph

Fig. 1.

$Os_3(CO)_{10}(RC_2R')_2$ (V); $Os_3(CO)_9(RC_2R')$ (VI); $HOs_3(CO)_9(R'C_2)$ (VII); $Os_3(CO)_9(RC_2R')_2$ (VIII); $HOs_3(CO)_8(RC_2Ph)[RC_2(C_6H_4)]$ (IX); $H_2Os_2(CO)_6(RC_2R')_2$ (X); and $Os_2(CO)_6(RC_2R')_2$ (XI). The relative yields of these complexes are sensitive to the nature of R and R'*.

Complexes IVa and IVb are analogous to the simple ethyne derivative V and are presumably isostructural. In n-octane under reflux complex IVa undergoes a H-atom transfer to give $HOs_3(CO)_9CCR'$ (VIIa) (Fig. 2) for which Ru analogues are known [6]. The complex VIa and VIb are analogous to $Fe_3(CO)_9(PhC_2Ph)$ and we have separated two isomeric forms of VIa as expected for the proposed structure (Fig. 2). Complex VIa isomerizes to VIIa in n-octane under reflux, suggesting that VIa is an intermediate in the transformation (IVa → VIIa + CO).

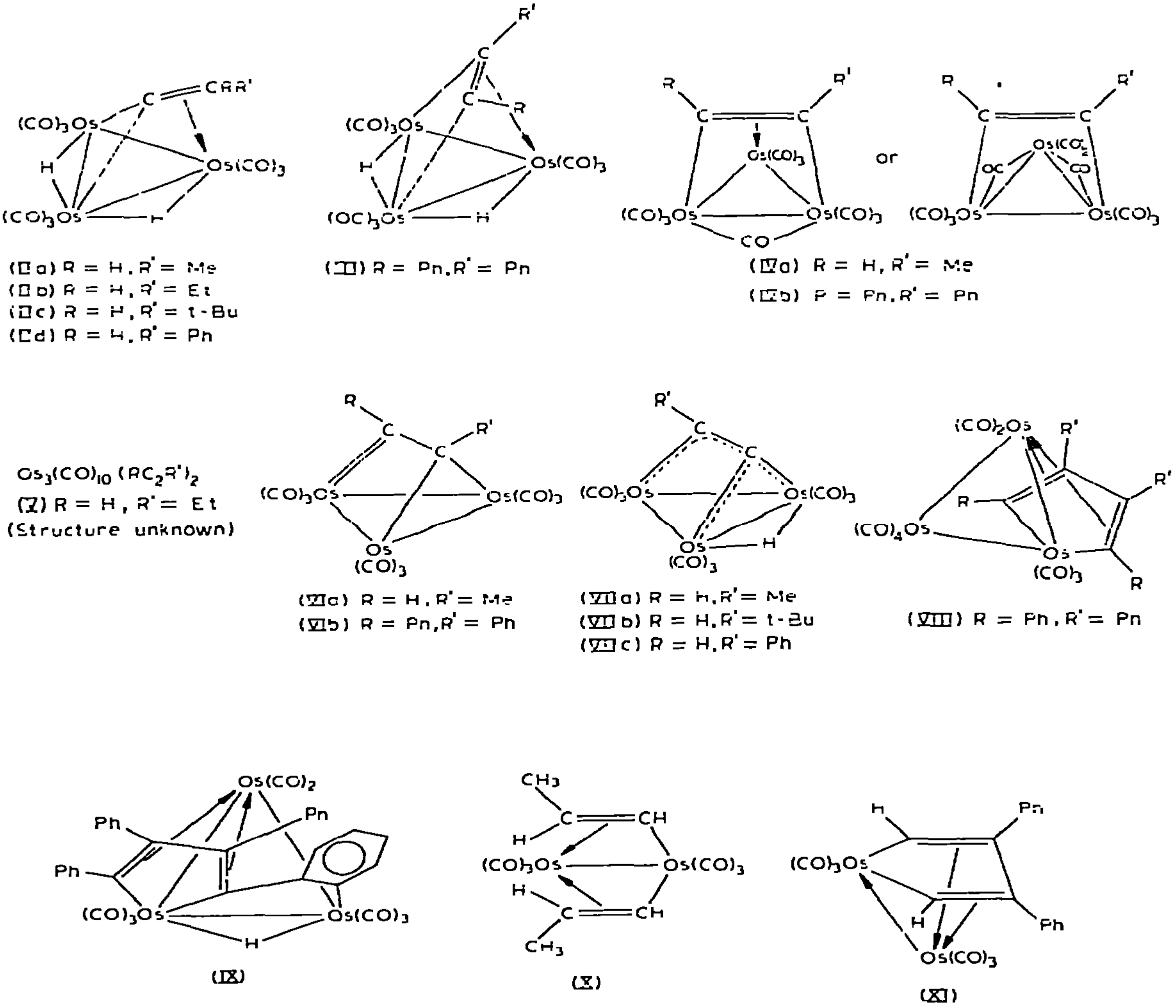


Fig. 2.

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*Significant yields (~60%) of $Os_3(CO)_9[(RC_2R')_2CO]$ in three separable isomeric forms are also obtained when R or R' = H; these compounds which have a novel structure are considered elsewhere.

The dinuclear complexes $Os_2(CO)_6(RC_2R')_2$ (XI) are similar to those reported [7] for Fe, Ru and Os. Two of the three possible isomers have been found for R = Ph, R' = H. Two isomers are also found for X. The proposed structures are tentative and several modes of isomerism can be envisaged.

The derivatives VIII and IX are identical to those reported [8-10] and can be interconverted by a reversible *ortho*-metallation reaction:

$$\underset{\text{(VIII)}}{Os_3(CO)_9(PhC_2Ph)_2} \xrightleftharpoons[+CO,\ 20^\circ]{\text{heat}} \underset{\text{(IX)}}{HOs_3(CO)_8(PhC_2Ph)[PhC_2(C_6H_4)]}$$

The complete sequence of reactions in this scheme is not clear. The formation of Os_2 complexes particularly under ambient conditions is surprising since the Os_3 cluster is normally robust. Several products correspond to the loss of H_2 and we have found that excess acetylene abstracts H_2 from complex I to yield VII. Similar dehydrogenations occur in ruthenium systems and with alkenes in related osmium systems, although they are less facile.

These results emphasize the variety of H-transfer processes possible in these systems several of which are reversible. The studies are being extended to recently synthesized higher osmium clusters [12].

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