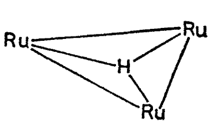
Cationic Polynuclear Carbonyl Hydrides of Ruthenium and Osmium

By J. KNIGHT and M. J. MAYS*

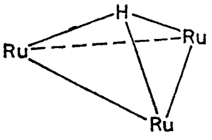
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The first cationic polynuclear carbonyl hydride complexes have been prepared.

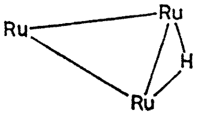
SOME metal carbonyl derivatives dissolve in strong acids, and n.m.r. studies on the resulting solutions have shown that, at least in some cases, protonation takes place leading to the formation of metal–hydrogen bonds.[1] The solutions frequently decompose rapidly and it is difficult to isolate the cationic species although a few, *e.g.* $[(\pi\text{-}C_5H_5)FeMn(CO)_7H]^+PF_6^-$ and $[HFe(CO)_5]^+PF_6^-$, have been obtained as solid salts.[1,2] The only previous attempt to protonate an unsubstituted polynuclear carbonyl complex [by dissolution of $Fe_3(CO)_{12}$ in $CF_3{\cdot}CO_2H$] led to rapid decomposition in solution.[1]



(Ia)



(Ib)



(Ic)

We now report that $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ give solutions in 98% H_2SO_4 which are stable for many days at room temperature even in the presence of air. Further, by careful addition of these solutions to concentrated aqueous solutions of ammonium hexafluorophosphate, air-stable cationic carbonyl hydride complexes can be isolated. These analyse satisfactorily as $[HRu_3(CO)_{12}]^+PF_6^-$ and $[HOs_3(CO)_{12}]^+PF_6^-$ and this formulation is in agreement with n.m.r. data for the sulphuric acid solutions, which show that only one proton is added per $M_3(CO)_{12}$ molecule (Table 1). The high-field n.m.r. lines can also be observed when the hexafluorophosphate salts are dissolved in acetone but slow deprotonation occurs in this solvent and the neutral carbonyls are reprecipitated. I.r. spectra of the hexafluorophosphate salts of the protonated carbonyl complexes have been recorded in nitromethane solution; the similarity of these spectra to those obtained for solutions of the parent carbonyls in trifluoroacetic acid indicates that the precipitated salts contain the same cations as those present in acid solutions. The presence of five carbonyl stretching absorptions in the i.r. spectra of the salts suggests a lowering of symmetry for these species from that of the parent carbonyls (D_{3h}) for which only four bands are predicted. This rules out structure (Ia) but does not distinguish between (Ib) (C_{3v} symmetry) and (Ic) (C_{2v} symmetry) for which seven and eleven bands respectively are allowed. It is interesting, however, that the related anion, $[H_2Re_3(CO)_{12}]^-$, for which an *X*-ray analysis suggests a C_{2v} structure analogous to (Ic), also shows five carbonyl absorptions.[3]

There is a second species formed on dissolution of $Os_3(CO)_{12}$ in sulphuric acid at room temperature which gives rise to an n.m.r. line at τ 30·2. This is present as a minor component initially but is the predominant species when the solution is

I.r. and n.m.r. spectra

Compound	Solvent	$\nu_{(C-O)}$	$\tau^*_{(M-H)}$	No. of protons†
$Ru_3(CO)_{12}$	n-Hexane	2060s, 2030s, 2010m		
$Ru_3(CO)_{12}$	$CF_3{\cdot}CO_2H$	2154s, 2135m, 2110s, 2089s, 2040m		
$Ru_3(CO)_{12}$	98% H_2SO_4		29·4	1
$Os_3(CO)_{12}$	n-Hexane	2070s, 2036s, 2015m, 2003m		
$Os_3(CO)_{12}$	$CF_3{\cdot}CO_2H$	2137s, 2107s, 2084s, 2066m, 2029m		
$Os_3(CO)_{12}$	98% H_2SO_4		29·9	1
$HRu_3(CO)_{12}{}^+PF_6{}^-$	$MeNO_2$	2129s, 2102s, 2081s, 2068sh, 2030m		
$HRu_3(CO)_{12}{}^+PF_6{}^-$	$CD_3{\cdot}CO{\cdot}CD_3$		28·6	
$HOs_3(CO)_{12}{}^+PF_6{}^-$	$MeNO_2$	2135s, 2102s, 2080s, 2061sh, 2021m		
$HOs_3(CO)_{12}{}^+PF_6{}^-$	$CD_3{\cdot}CO{\cdot}CD_3$		29·1	

* Chemical shift values referred to Me_2SO_4 in H_2SO_4. $\tau_{(C-H)}$ for Me_2SO_4 taken as 6·1.

† Estimated by comparison with the resonance from weighed amounts of Me_2SO_4.

heated at 100° for a few hours. Addition of this solution to water causes the precipitation of a mixture of carbonyl-containing species which have not yet been characterised but since the parent carbonyl, $Os_3(CO)_{12}$, cannot be regenerated, it is clear that loss of CO groups and/or breaking of the metal–metal bonds has occurred.

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[1] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.
[2] Z. Iqbal and T. C. Waddington, *J. Chem. Soc.* (*A*), 1968, 2958.
[3] R. Bau, P. H. Bird, M. R. Churchill, B. Fontal, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1968, **90**, 7135.