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Preliminary communication

PREPARATION OF SOME METAL CARBONYL CLUSTER FORMYL COMPOUNDS

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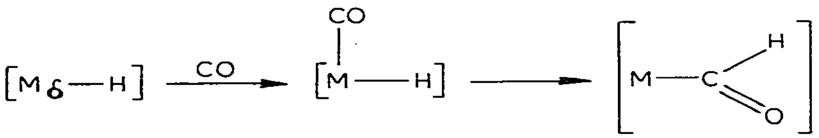
Summary

The reduction of $H_2Os_3(CO)_{10}S$ or $HOs_3(CO)_{10}(O_2CMe)$ with $KBH(OPr\text{-}i)_3$ at low temperatures yields unstable formyl complexes which have been identified by ^1H NMR spectroscopy; at higher temperatures conversion into stable hydrido-anions is observed.

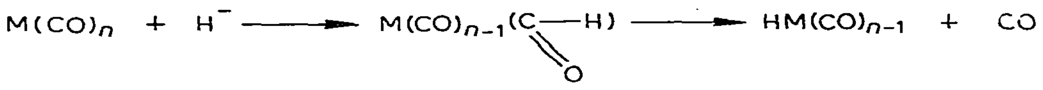
Introduction

The recent communication by Pruett, Schoening, Vidal and Fiato [1] prompts us to report our investigations into the synthesis and characterisation of formyl-metal cluster complexes. This work was initiated in order to more fully investigate the mechanism for Fischer—Tropsch reductive hydrogenation of carbon monoxide, proposed by Olivé and Olivé [2], in which the insertion of carbon monoxide into a metal hydrogen bond to produce a formyl complex is considered to be the initial step:



Results and discussion

In recent years we have examined [3] the reduction of a variety of neutral cluster carbonyl systems with sodium borohydride. In all cases, under the conditions employed, hydrido-carbonyls were the products. In work on monometal systems Casey [4] demonstrated that in some cases at least, the initial attack by H^- occurred directly on coordinated CO to give a formyl derivative, followed by migration to the metal and CO ejection.

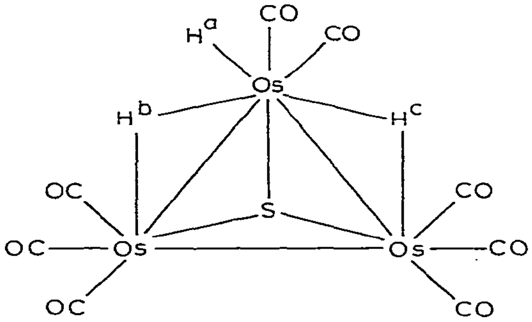


$$M(CO)_n + H^- \longrightarrow M(CO)_{n-1}(\overset{\displaystyle \ }{C}(=O)H) \longrightarrow HM(CO)_{n-1} + CO$$

(eg. $Fe(CO)_5$)

Using a more active reducing agent $K(HB(OR)_3)$ Casey was able to isolate the formyl intermediate complexes by carrying out the reduction at low temperatures.

This work is an extension of these ideas to cluster systems; five have been chosen to give information on systems in which there is large steric interaction about the metal cluster unit, in an attempt to direct attack primarily to the carbonyl groups and reduce the probability of transfer to the metal centre. Thus the S-capped complex $H_2Os(CO)_9S$ reacts with $NaBH_4$ in tetrahydrofuran at room temperature to produce, in good yields, the anionic cluster $HOs_3(CO)_9S^-$ and hydrogen. On reduction with $KHB(OPr\text{-}i)_3$ at −10°C, the complex reacts to give a complex which exhibits a resonance at τ −5.07 in the ^1H NMR. On warming to 0°C this signal slowly disappears and is replaced by new signals which correspond to the anionic species $[H_3Os_3(CO)_8S]^-$ and $[HOs_3(CO)_9S]^-$. These anionic clusters were isolated as their salts and characterised by analysis and spectroscopy. The trihydrido species is new, and is considered to contain both terminal and bridged H-ligands:



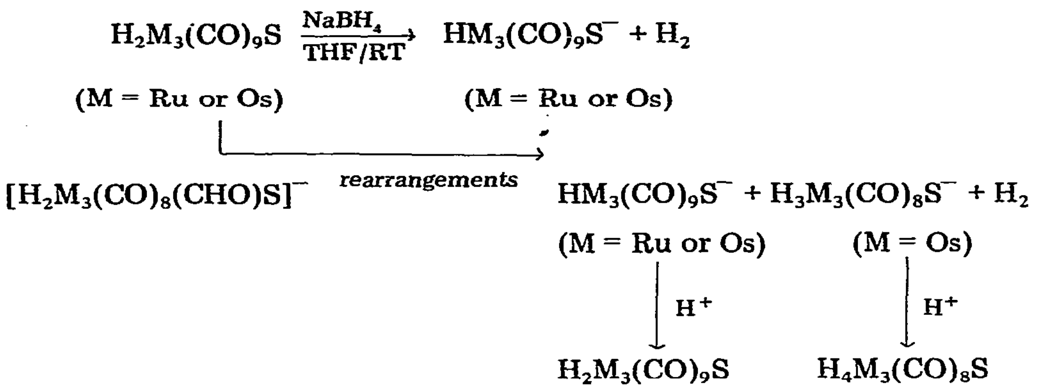
H^a τ 23.95, $J(H^a-H^c)$ 13.31 Hz

H^b τ 31.03, $J(H^a-H^b)$ 2.39 Hz

H^c τ 29.29, $J(H^b-H^c)$ 0 Hz

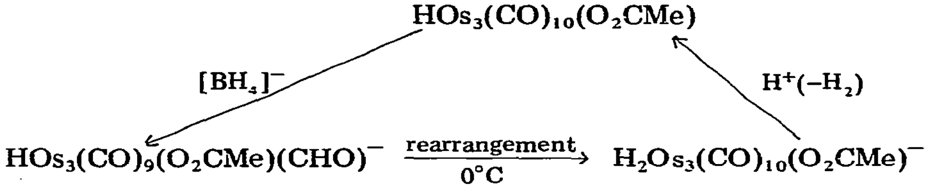
The terminal hydrido-ligand H^a is considered to be bonded *trans* to the bridge H^c in view of the comparatively large coupling constant and *cis* to H^b. Acidification of these anions leads to the formation and isolation of the neutral hydrido compounds $H_4Os_3(CO)_8S$ and $H_2Os_3(CO)_9S$. The corresponding ruthenium complex, $H_2Ru_3(CO)_9S$ reacts similarly to produce a formyl derivative but at lower temperatures (−60°C). In this case when the temperature is raised only one product, $HRu_3(CO)_9S^-$, is observed and on acidification this yields $H_2Ru_3(CO)_9S$.

The reaction of $HOs_3(CO)_{10}(O_2CMe)$ with $[PPN][BH_4]$ in CD_2Cl_2 at −40°C proceeds rapidly to give a deep orange solution. The ^1H NMR spectrum of this solution shows to resonances at τ −5.12 and 20.00. On this basis we conclude that the formyl complex $HOs_3(CO)_9(CHO)(O_2CMe)^-$ (A) has been generated. As the temperature is raised to 0°C the formyl and hydride resonances due to A disappear, and we propose that $H_2Os_3(CO)_{10}(O_2CMe)^-$ is generated by hydride migration from the formyl group on to the metal. The identity of this species is based on its frozen out ^1H NMR spectrum at −40°C, in which there are two



coupled hydride resonances at τ 20.08 and 25.91 (J(H—H) 4.2 Hz), and on the experimental observation that acidification regenerates $HOs_3(CO)_{10}(O_2CMe)$ in good yield.

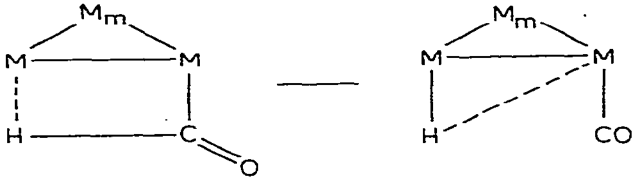
An experiment in which the reaction between $HOs_3(CO)_{10}(O_2CMe)$ and [PPN][BH_4] was monitored at −20°C by infrared spectroscopy revealed a band at 1606 cm^{-1} (CH_2Cl_2 solvent). Tentatively this might be assigned to ν(C=O) of the formyl group, but caution must be observed, since acetate ν(C=O) stretches occur in this region (e.g. $HOs_3(CO)_{10}(O_2CMe)$ has a band at 1550 cm^{-1}).



The reaction with $KHB(OPr\text{-}i)_3$ at −70°C produces two complexes which exhibit formyl resonances at τ −5.12 and −6.00, respectively. As the temperature is raised above −10°C the signals due to complex (B) (τ −6.00 and 19.29) disappear more quickly than those due to A. Almost certainly the complex anions A and B are isomers.

Further studies have shown that reaction of $KBH(OPr\text{-}i)_3$ with $Os_3(CO)_{12}$ leads to the formation of an unstable formyl complex which undergoes rearrangement to produce the hydrido-anion ($HOs_3(CO)_{11}^-$). In other cases, e.g. $Fe_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $Ru_3(CO)_{12}$ and $Ru_6C(CO)_{17}$, the formation of anionic compounds occurs and no spectroscopic evidence for the formation of intermediate formyls has been obtained.

In conclusion we also note that the stability of cluster formyl complexes is lower than that of the related monometal species. We would suggest that this instability is associated with the availability of an "α-elimination" mechanism in cluster systems:



related to the β-elimination observed in mononuclear systems.

References

1 R.L. Pruett, R.C. Schoening, J.L. Vidal and R.A. Fiato, J. Organometal. Chem., 182 (1979) C57.
2 G.H. Olivé and S. Olivé, Angew. Chem. Int. Ed. Engl., 15 (1976) 136.
3 See for example B.F.G. Johnson, J. Lewis, P.R. Raithby, G.M. Sheldrick and G. Süss, J. Organometal. Chem., 162 (1978) 179.
4 C.P. Casey and S.M. Neumann, J. Amer. Chem. Soc., 98 (1976) 5395.