Journal of Organometallic Chemistry, 444 (1993) C51–C52

JOM 23224PC

Preliminary Communication

The controlled assembly of high nuclearity osmium clusters from smaller fragments

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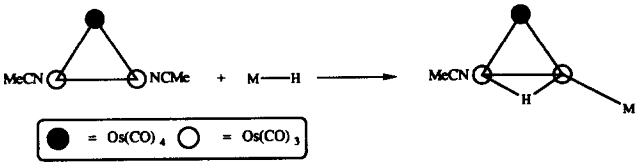
(Received July 1, 1992)

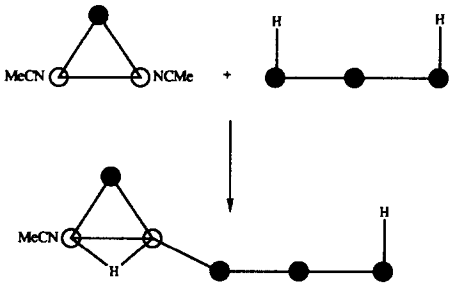
Abstract

The step-wise assembly of larger osmium clusters can be accomplished by addition of $Os_3(CO)_{10}(MeCN)_2$ to the dihydrides $H_2[Os(CO)_4]_n$ ($n = 1$ to 3).

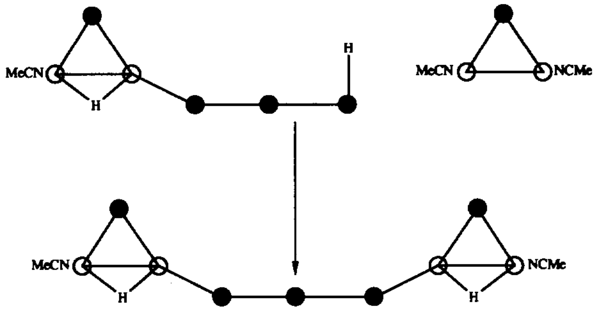
The controlled synthesis of large clusters of a particular nuclearity is a conspicuous challenge. Many existing synthetic routes give mixtures of clusters with a wide range of nuclearities that can be difficult to separate and the yields of which are often variable [1]. The reaction of the triangular acetonitrile substituted cluster $Os_3(CO)_{10}(MeCN)_2$ with mononuclear metal hydrides has been previously shown to yield "spiked" clusters where M–H = $HRe(CO)_5$ [2] or $H_2Os(CO)_4$ [3] in good yields. The "spiked" tetranuclear cluster, where M=$HOs(CO)_4$ did not react with an excess of $H_2Os(CO)_4$ to give a pentanuclear complex [3].



We now show that the hydrides of the homologous series $H_2[Os(CO)_4]_n$ ($n = 1$, 2 or 3) [4] will add one or two molecules of $Os_3(CO)_{10}(MeCN)_2$ in a stepwise fashion. Thus, the reaction of $Os_3(CO)_{10}(MeCN)_2$ with $H_2Os_3(CO)_{12}$ (in a 1 : 1 molar ratio) in dichloromethane at room temperature for 30 min yields the 3 + 3 addition product **1** as the major product in good yield.



(1)



(2)

An analogous addition of $Os_3(CO)_{11}(MeCN)$ to $H_2Os_3(CO)_{12}$ occurs in a slower reaction. Compound **1** * was isolated as an orange solid after working up the reaction mixture by thin layer chromatography. The chemical shift of the terminal Os–H in the ^1H NMR and the observation that **1** readily reacts with CCl_4 to give $HClOs_6(CO)_{22}(MeCN)$ ** suggest that the reactivity of the terminal Os–H bond in **1** may be similar to that of the starting dihydride $H_2Os_3(CO)_{12}$. Indeed, reaction of **1** with $Os_3(CO)_{10}(MeCN)_2$ in dichloromethane at room temperature for 1 h yields the addition product **2** as shown.

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* IR $\nu(CO)$ (CH_2Cl_2): 2127w, 2101m, 2084w, 2063m, 2053m, 2028vs, 2010sh, 1957wbr cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.56 (MeCN), δ −9.85 (terminal Os–H), δ −16.74 (bridging Os–H). The mass spectrum shows a parent ion at m/e 1801 in agreement with the formulation $H_2Os_6(CO)_{22}(MeCN)$.

** IR $\nu(CO)$ (CH_2Cl_2): 2122w, 2106w, 2061vs, 2022vs cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.52 (MeCN) δ −16.83 (bridging Os–H). The mass spectrum shows a parent ion at m/e 1835.

0022-328X/93/$6.00

Compound **2** *** can also be obtained directly by the reaction of $Os_3(CO)_{10}(MeCN)_2$ and $H_2Os_3(CO)_{12}$ in a 2:1 molar ratio. Thus the Os_9 species, the result of a 3 + 3 + 3 addition, is assembled from two triangular Os_3 end groups and a linear Os_3 link. We have also demonstrated that the linking fragment can be varied. Thus $Os_3(CO)_{10}(MeCN)_2$ reacts with $H_2Os_2(CO)_8$ in dichloromethane at room temperature to yield the anticipated 3 + 2 addition product, $H_2Os_5(CO)_{18}(MeCN)$ † and the 3 + 2 + 3 addition product, $H_2Os_8(CO)_{28}(MeCN)_2$ ††. Similarly, $Os_3(CO)_{10}(MeCN)_2$ reacts with $H_2Os(CO)_4$ to yield the new 3 + 1 + 3 addition product $H_2Os_7(CO)_{24}(MeCN)_2$ ††† as well as the known 3 + 1 addition product $H_2Os_4(CO)_{14}(MeCN)$ [3].

We have also demonstrated that the end groups can be varied, and have obtained addition porducts with $Os_3(CO)_{11}(MeCN)$ as well as with $Ru_3(CO)_{10}(MeCN)_2$. Thus with the ability to change the end groups and the linking groups as well as to isolate the intermediates such as compound **1**, this method gives an efficient and versatile way of assembling a wide range of homo- ‡ and heterometallic clusters from smaller fragments. We are currently exploring the scope of this reaction as well as investigating the closing-up of the clusters thus obtained, as was observed for the spiked cluster $H_2Os_4(CO)_{14}(MeCN)$ [3].

Acknowledgements

We thank the University of Cape Town and the F.R.D. for support to J.R.M.

References

1 M. D. Vargas and J. N. Nicholls, *Adv. in Inorg. Chem. Radiochem.*, *30* (1986) 123.
2 M. R. Churchill, F. J. Hollander, R. A. Lashewycz, G. A. Pearson and J. R. Shapley, *J. Am. Chem. Soc.*, *103* (1981) 2430.
3 E. J. Ditzel, B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1985) 555.
4 J. R. Moss and W. A. G. Graham, *Inorg. Chem.*, *16* (1977) 75.

*** IR ν(CO) (CH_2Cl_2): 2101m, 2092sh, 2060s, 2025sh, 2015vsbr. ^{1}H NMR (CD_2Cl_2): δ 2.58 (MeCN), δ −16.62 (bridging Os–H). +ve FAB mass spectrum showed a parent ion at *m/e* 2693 in agreement with the formulation $H_2Os_9(CO)_{32}(MeCN)_2$.

† IR ν(CO) (CH_2Cl_2): 2123w, 2095m, 2071sh, 2060s, 2026 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.53 (MeCN), δ −9.96 (terminal Os–H), δ −16.76 (bridging Os–H). The mass spectrum shows a parent ion at *m/e* 1499.

†† IR ν(CO) (CH_2Cl_2): 2117w, 2098m, 2085m, 2064s, 2050m, 2025s, 2012sh, 2007 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.57 (MeCN), δ −16.62 (bridging Os–H). The mass spectrum shows a parent ion at *m/e* 2390.

††† IR ν(CO) (CH_2Cl_2): 2093m, 2076m, 2059s, 2025vs, 2006sbr, 1984 mbr cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.56 (MeCN), δ −16.59 (bridging Os–H). The mass spectrum shows a parent ion at *m/e* 2088.

‡ Just using the end group $Os_3(CO)_{10}(MeCN)_2$ and the link groups $H_2[Os(CO)_4]_n$ (n = 1, 2 or 3) it is possible to assemble all nuclearities from 4 to 9 by at least one route: *i.e.* 3+1, 3+2, 3+3, 3+1+3, 3+2+3, 3+3+3.