

Preliminary communication

PREPARATION OF UNDECACARBONYLTRIOSMIUM DERIVATIVES

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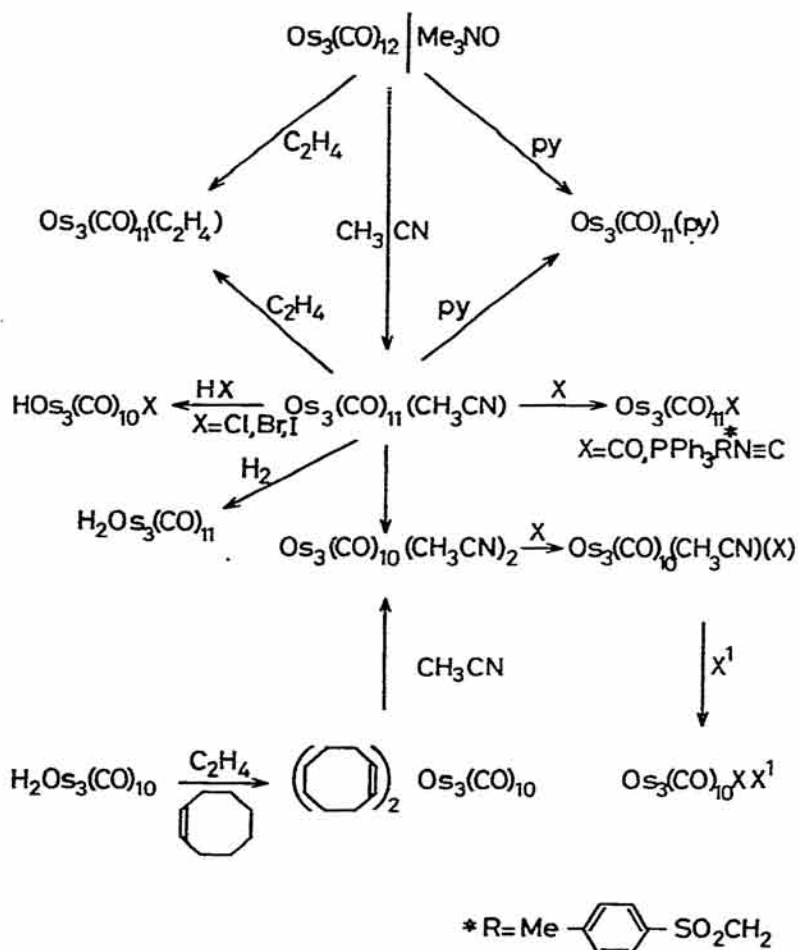
Summary

Undecacarbonyltriosmium derivatives have been prepared by treatment of dodecacarbonyltriosmium with amine oxide in low ratio (1/1). Substitution reactions with halogen acids lead to $\text{HOs}(\text{CO})_{11}\text{X}$ derivatives which readily lose carbon monoxide to yield $\text{HOs}_3(\text{CO})_{10}\text{X}$ compounds.

Substitution reactions of dodecacarbonyltriosmium have mainly been carried out accomplished by thermal or photochemical methods. These often lead to a complexity of products. Recently we suggested the use of the complex $(\text{C}_6\text{H}_8)\text{Os}_3(\text{CO})_{10}$ [1] as a reagent for the preparation of decacarbonyl derivatives, since the cyclohexadiene ligand can be displaced under relatively mild conditions. Subsequently Shapley [2], suggested as an alternative for the preparation of the decacarbonyl complexes, the bis(acetonitrile)decacarbonyltriosmium complex $(\text{CH}_3\text{CN})_2\text{Os}_3(\text{CO})_{10}$, prepared via the cyclooctene/ethylene reaction with the hydrido carbonyl $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (see Scheme 1). We have been able to prepare the same acetonitrile derivative utilising trimethylamine oxide as the primary activator of the parent carbonyl. Reaction occurs under mild conditions to give the product $(\text{CH}_3\text{CN})_2\text{Os}_3(\text{CO})_{10}$ in good yield. The successive replacement of the two acetonitrile groups, observed by Shapley and by us, provides a useful entry into the mixed decacarbonyl derivatives.

Using trimethylamine oxide in a lower amine oxide to osmium carbonyl mole ratio (1/1) it is possible to isolate the monosubstituted acetonitrile derivative $(\text{CH}_3\text{CN})\text{Os}_3(\text{CO})_{11}$ in high yields (~85%), which is an extremely useful reagent for the preparation of the undecacarbonyl adducts. Scheme 1 illustrates a number of the reactions that have been carried out. With ethylene and pyridine the reaction occurs smoothly with the amine oxide/dodecacarbonyl directly to give the monosubstituted derivatives, but with acid or other reagents which may also react with the amine oxide it is convenient to prepare the intermediate acetonitrile derivative.

The pyridine and ethylene complexes have been postulated as primary products in the interaction of these reagents with the dodecacarbonyl, which yield



SCHEME 1

the adducts $\text{HOs}_3(\text{CO})_{10}(\text{NC}_5\text{H}_4)$ (I) [3] and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)$ (II) [4]. In agreement with this they are smoothly converted into I and II, respectively, on refluxing in octane in the presence of the ligand. For the ethylene complex it is not possible to isolate the other proposed intermediate, the vinyl adduct $\text{HOs}_3(\text{CO})_{10}(\text{CH}=\text{CH}_2)$. The ethylene compound is the first reported monosubstituted π -bonded olefin derivative of a trinuclear cluster.

The ease of displacement of the acetonitrile group makes $(\text{MeCN})\text{Os}_3(\text{CO})_{11}$ very useful in preparing a variety of compounds which are potential intermediates in substitution reactions of the parent carbonyl and which appear to be unstable under the reaction conditions employed with this carbonyl. Thus reaction of the acetonitrile complex with halogen acids gives initially in the case of chloride and bromide the undecacarbonyl adducts $\text{HOs}_3(\text{CO})_{11}\text{X}$ which readily lose carbon monoxide to yield the well-known decacarbonyl adducts $\text{HOs}_3(\text{CO})_{10}\text{X}$. Hydrogen iodide leads to the equivalent decacarbonyl adduct, as the undecacarbonyl adduct appears to be a less stable intermediate.

The acetonitrile complex thus provides a convenient reagent for the preparation of a variety of undecacarbonyl adducts. The reactions with other substrates will be reported in full later, but we should mention that we have in particular investigated the reaction of the complex with alkynes, which yield a novel series of compounds.

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