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Synthesis and characterisation of $[HOs_3(CO)_{10}$-$(\mu$-$TeC_6H_4OMe)]$ and its conversion into $[Os_3Te_2(CO)_9]$

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Abstract

The synthesis of $[HOs_3(CO)_{10}(\mu$-$TeC_6H_4OMe)]$ by the room temperature reaction of $[HOs_3(CO)_{11}][PPN]$ with $\{(OMe)C_6H_4\}_2TeCl_2$, and its conversion into $[Os_3Te_2(CO)_9]$ under thermolysis are described.

Introduction

The coordinating properties of the bridging sulfido group has been utilised for the synthesis of a variety of high nuclearity sulfido osmium carbonyl cluster compounds, as well as for the synthesis of a number of mixed metal carbonyl cluster compounds [1]. The structures of some of these large cluster compounds epitomize the differences between the simple 18 electron rule and the polyhedral skeletal electron pair theory for explaining the bonding in cluster compounds. A convenient starting material for obtaining sulfido osmium clusters is $[HOs_3(CO)_{10}(\mu$-$SCH_2Ph)]$, which, under thermolysis at 150 °C has been shown to yield the clusters $Os_6(CO)_{16}(\mu_4$-$S)(\mu_3$-$S)$, two isomers of $H_2Os_6(CO)_{17}(\mu_4$-$S)(\mu_3$-$S)$, $Os_7(CO)_{20}(\mu_4$-$S)_2$, and a trace of $Os_3S_2(CO)_9$ [2]. The last of these products has been shown to add metal carbonyl fragments to form several larger cluster compounds in a systematic way [3–5]. Until recently the chemistry of tellurium-containing clusters has not attracted as much attention, probably because of the belief that the behaviour of tellurium would be identical with that of the well studied sulfur in directing the synthesis of larger cluster compounds and also because of the relative paucity of convenient tellurium-containing starting materials. However, the work carried out by Rauchfuss [6,7] and the recent studies in our laboratory [8,9] show that tellurium imparts contrasting and interesting properties to the complexes into which it is incorporated. For instance, whereas a large number of the sulfido osmium clusters reported have closed structures, the larger tellurium atom prevents

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new metal–metal bond formation during cluster growth and thus cluster compounds having open structures result. Here we report the synthesis and characterisation of the novel compound $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$, and of $[Os_3Te_2(CO)_9]$, both of which can serve as starting materials for high nuclearity tellurium-containing cluster compounds in the same manner as shown by the related sulfur containing molecules, $[HOs_3(CO)_{10}(\mu\text{-}SCH_2Ph)]$ and $[Os_3S_2(CO)_9]$.

Results and discussion

A mixture of $[HOs_3(CO)_{11}][PPN]$ and $\{(OMe)C_6H_4\}_2TeCl_2$ in dichloromethane, with stirring at room temperature for 24 hours yielded the neutral compound $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$, which was characterised by infrared and NMR spectroscopy and by microanalysis. The infrared spectrum of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ in the carbonyl region displays bands at 2105 (m), 2064 (s), 2055 (m) 2024 (s), 2009 (s), 1999 (m), 1985 (w) cm^{-1} and it closely resembles the spectra for the related compounds, $[HOs_3(CO)_{10}(\mu\text{-}X)]$, ($X=SC_2H_5$, SC_6H_5, SC_4H_9). The ^1H NMR spectrum of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ in $CDCl_3$ exhibits a resonance at τ 28.81, which confirms the presence of a bridging hydrido atom as suggested in the structure shown in Fig. 1. The resonance at τ 6.2 may be attributed to the presence of the –OMe group while the resonances at τ 3.1–3.3 and 2.3–2.5 are attributable to the $-C_6H_4$ group. Microanalysis confirms the molecular formula $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$. (Analysis: Found; C, 18.92; H, 0.84. $C_{17}H_8Os_3O_{11}Te$ Calc: C, 18.79: H, 0.73%). When refluxed in octane solvent for 1–2 hours, $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ was transformed into the known cluster $[Os_3(CO)_9(\mu_3\text{-}Te)_2]$ which was identified from its IR data [10].

The complexes $[HOs_3(CO)_{10}(\mu\text{-}X)]$ are members of a series of compounds having similar physical properties and virtually identical NMR and IR data and so it was possible to conclude from the known structures of $[Os_3(CO)_{10}(\mu\text{-}OMe)_2]$ and $[H_2Os_3(CO)_{10}]$ (Fig. 2) that the members of the above mentioned series all have similar structures [11]. The similarity of the carbonyl regions in the IR spectra of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ and $[HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)]$ is depicted in Fig. 3. Typically, the complexes $[HOs_3(CO)_{10}(\mu\text{-}SR)]$ have been prepared by refluxing dodecacarbonyltriosmium with the thiols, RSH in benzene or toluene solvent. The absence of the tellurium derivative, RTeH, precludes the use of the same procedure to make the tellurium analogues, $[HOs_3(CO)_{10}(\mu\text{-}TeX)]$. Our method of preparing the compound $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ at room temperature should serve as a model for the preparation of the series of compounds having the general formula

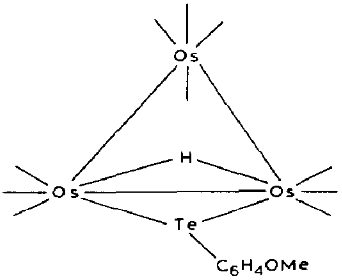

Fig. 1. Proposed structure of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$.

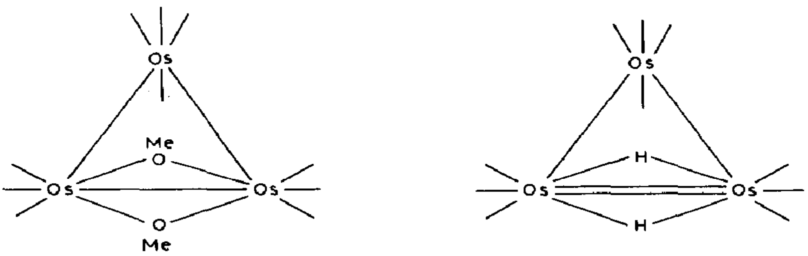

Fig. 2. Structures of the known compounds $[Os_3(CO)_{10}(\mu\text{-}OMe)_2]$ and $[Os_3(CO)_{10}(\mu\text{-}H)_2]$.

$$[HOs_3(CO)_{11}][PPN] + \{(OMe)C_6H_4\}_2TeCl_2 \rightarrow$$

$$[HOs_3(CO)_{10}Te\{(OMe)C_6H_4\}] + \text{other clusters}$$

$$[HOs_3(CO)_{10}Te\{(OMe)C_6H_4\}] \xrightarrow{\Delta} [Os_3(\mu_3\text{-}Te)_2(CO)_9]$$

Scheme 1. Formation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}TeC_6H_4OMe)]$ and its conversion into $[Os_3(CO)_9(\mu_3\text{-}Te)_2]$.

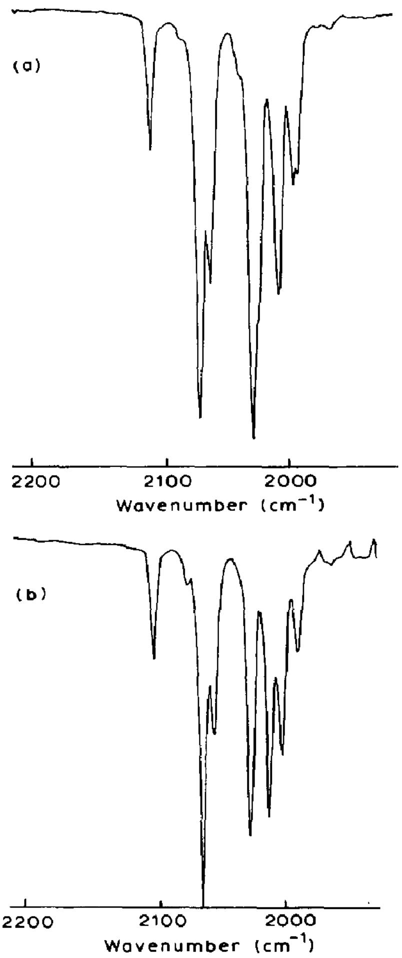

Fig. 3. Infrared spectra in the carbonyl region in hexane solvent of (a) $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SPh)]$ and (b) $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}TeC_6H_4OMe)]$.

$[HOs_3(CO)_{10}(\mu\text{-}TeX)]$ (Scheme 1.) The conversion of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ into $[Os_3(CO)_9(\mu_3\text{-}Te)_2]$ under thermolytic conditions is a better route to $[Os_3(CO)_9(\mu_3\text{-}Te)_2]$ than the previously reported method that involves high temperatures and pressures.

Experimental

All reactions were carried out under prepurified argon by use of standard Schlenk techniques. Solvents were purified and dried before use. The compounds $[HOs_3(CO)_{11}][PPN]$ [12] and $\{(OMe)C_6H_4\}_2TeCl_2$ [13] were prepared by published procedures. The infrared spectra were recorded on a Nicolet 5DXB Fourier transform infrared spectrometer, NMR spectra were recorded on a Bruker-80 FT NMR spectrometer as $CDCl_3$ solutions, with TMS as internal standard. The microanalysis was performed by a Carlo Erba automatic analyser.

Preparation of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$

To a dichloromethane solution (20 ml) of $[PPN][HOs_3(CO)_{11}]$ (0.2 g, 0.14 mmol) was added $\{(OMe)C_6H_4\}_2TeCl_2$ (0.06 g, 0.15 mmol) and the mixture was stirred for 24 hours. The solvent was removed in vacuo and the residue was put on silica gel TLC plates. Elution with a mixture of hexane and dichlorometane (80 : 20 v/v) separated the yellow $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ from traces of as yet unidentified compounds. Recrystallisation by slow evaporation of the dichloromethane/hexane solvent gave orange crystals of the product (yield 11 mg, 7%).

Preparation of $[Os_3Te_2(CO)_9]$

A solution of $[HOs_3(CO)_{10}(\mu\text{-}TeC_6H_4OMe)]$ (0.016 g, 0.014 mmol) in 20 ml of octane was refluxed for 2 hours. The solvent was then removed in vacuo. The residue was extracted with hexane and applied to silica TLC plates. Elution with hexane afforded the yellow band of $Os_3Te_2(CO)_9$ (yield 1 mg, 6%).

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